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AN INTRODUCTION  
TO  
ORGANIC CHEMISTRY

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AN INTRODUCTION  
TO  
ORGANIC CHEMISTRY

BY

ALEXANDER LOWY, PH.D.

*Professor of Organic Chemistry, University of Pittsburgh*

AND

BENJAMIN HARROW, PH.D.

*Associate Professor of Chemistry, College of the  
City of New York*

THIRD EDITION

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1932

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BY ALEXANDER LOWY

AND

BENJAMIN HARROW

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## PREFACE TO THIRD EDITION

THE very cordial reception which the first two editions of this book have received at the hands of the teaching and student body has prompted us to take the opportunity offered by the publishers to prepare a new edition. Since the appearance of the second edition four years ago, several important advances have been made in organic chemistry. Perhaps the most striking, and in many ways an unexpected advance, has dealt with the aliphatic series of compounds. A new chart—the development of products derived from ethylene—as well as a number of additions in the first part of the book, are evidence of this striking advance. Newer conceptions of sugar structure, a synthesis of sucrose, and the artificial production of a rubber-like substance may also be mentioned. But it may be said, in general, that the more important recent advances in the field of organic chemistry have been included—at least, such of them as can be included in an elementary text; and the reading references have also been brought up to date.

Our thanks are due to many friends for advice and criticism.

ALEXANDER LOWY.

BENJAMIN HARROW.

January, 1932.





## PREFACE TO FIRST EDITION

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IN the preparation of this work the authors have tried to keep a number of objects constantly in mind. In the first place, they desired to embody in the work material which could be satisfactorily treated in a course in which the theory of organic chemistry is covered in two semesters (two hours a week). They were also anxious that such material should include not only the well-recognized basic principles of organic chemistry, but also its more recent and more important applications; the entire story being woven together into a simple and readable narrative.

The authors have also kept in mind the many connecting links that bind organic chemistry to a number of other sciences,—to medicine, dentistry, pharmacy; to agriculture; to the biological sciences; hence, the inclusion of such chapters as those dealing with lipoids; nucleoproteins and their decomposition products; the chemical changes which foodstuffs undergo in the body; plant and animal pigments; enzymes, vitamins and hormones; organic compounds of arsenic and other metals; dyes and stains, etc.

The text can, therefore, be appropriately used in connection with a lecture course, not only by the student who is taking organic chemistry as part of a general academic course, or as preparation for a more extended course in chemistry, but by one who is preparing for the medical, dental, pharmaceutical or other biological sciences.

The book is not intended to act as a guide for laboratory manipulations; details for the preparation of compounds are, therefore, intentionally omitted. Neither, with a few exceptions, are boiling points, melting points or other physical constants included in the body of the work; some of these will be found in the form of a table in the appendix.

To aid the student in naming organic compounds, a brief chapter (XXXVII) is devoted to this topic.

The structure of benzene and its derivatives is shown in

heavy and light lines, the heavy lines representing double bonds. This is in accordance with a plan originally proposed by one of the authors.<sup>1</sup>

The two colored charts, taken in conjunction with Chapter XXXIV (a brief outline for the identification of organic substances), should serve, to some extent, the purposes of a review.

A number of charts throughout the text, illustrating the uses of a few important chemicals, have been incorporated if only to give the student some idea of the many and diverse uses to which organic substances may be put.

In the opinion of the authors, the student should at the very outset be given some opportunity for collateral reading; hence, the references at the end of chapters and the general references at the end of the book.

The glossary has been added to explain a number of medical terms used in the text.

Photographs of a few of the outstanding leaders in organic chemistry have been included.

The authors have freely consulted various text-books and journals and they wish to acknowledge their debt to the men responsible for the texts and articles.

For their kindness in giving permission to reproduce diagrams, the authors wish to thank the following: The Marland Oil Co. (Petroleum Refining); R. F. Remler of the Mellon Institute of Industrial Research, and the National Wood Chemical Association (Uses of Methanol, Uses of Acetic Acid, Uses of Acetone, Uses of Formaldehyde); The U. S. Industrial Alcohol Co. (Ethyl Alcohol); D. Van Nostrand Co. (two colored charts); and Cain and Thorpe: "Synthetic Dyestuffs and Intermediate Products" (Substituents in Naphthalene Ring).

The authors are indebted to Dr. Tesh for complete proof-reading and to other members of the Department of Chemistry of the University of Pittsburgh for criticism.

The authors will at all times welcome suggestions and criticism.

ALEXANDER LOWY.  
BENJAMIN HARROW.

<sup>1</sup>*Journal of the American Chemical Society*, **41**, 1029 (1919).

# CONTENTS

	PAGE
PREFACE TO THIRD EDITION.....	v
PREFACE TO FIRST EDITION.....	vii
NOTE FOR STUDENT.....	xi
REPLACEMENT OF ELEMENTS AND GROUPS.....	xiii

## ALIPHATIC SERIES

### CHAPTER

I. INTRODUCTION.....	1
II. SATURATED HYDROCARBONS OR PARAFFINS AND PETROLEUM.....	18
III. UNSATURATED HYDROCARBONS OR OLEFINS AND ACETYLENES.....	31
IV. HALOGEN DERIVATIVES OF HYDROCARBONS.....	41
V. ALCOHOLS.....	49
VI. ETHERS.....	69
VII. ALDEHYDES AND KETONES.....	73
VIII. ACIDS.....	85
IX. SALTS AND ESTERS OF INORGANIC AND ORGANIC ACIDS.....	96
X. FATS AND OILS, WAXES AND LIPOIDS.....	105
XI. ACID ANHYDRIDES, ACYL HALIDES AND ACID AMIDES.....	113
XII. HALOGEN SUBSTITUTED ACIDS AND HYDROXY ACIDS.....	123
XIII. AMINES OR ORGANIC BASES.....	138
XIV. AMINO ACIDS AND PROTEINS.....	143
XV. NUCLEOPROTEINS, PURINES, URIC ACID AND PYRIMIDINES.....	155
XVI. CYANIDES, ISOCYANIDES AND OTHER NITROGEN COMPOUNDS.....	160
XVII. CARBOHYDRATES AND RELATED COMPOUNDS.....	166
XVIII. FOODSTUFFS AND THEIR CHANGES IN THE BODY.....	186
XIX. SULFUR, PHOSPHORUS, ARSENIC AND ORGANO-METALLIC COMPOUNDS.....	194

## AROMATIC SERIES

XX. INTRODUCTION TO CYCLIC COMPOUNDS.....	200
XXI. CONSTITUTION OF BENZENE AND THE AROMATIC HYDROCARBONS.....	203
XXII. HALOGEN DERIVATIVES, SULFONIC ACIDS AND NITRO COMPOUNDS OF THE AROMATIC HYDROCARBONS.....	222
XXIII. AROMATIC AMINES, DIAZO AND AZO COMPOUNDS.....	234
XXIV. AROMATIC ALCOHOLS, PHENOLS AND ETHERS.....	248
XXV. AROMATIC ALDEHYDES, KETONES AND QUINONES.....	259
XXVI. AROMATIC ACIDS AND THEIR DERIVATIVES.....	268

CHAPTER	PAGE
XXVII. ADDITIONAL AROMATIC COMPOUNDS CONTAINING MIXED GROUPS.....	277
✓XXVIII. NAPHTHALENE, ANTHRACENE AND THEIR DERIVATIVES.....	294
XXIX. HETEROCYCLIC COMPOUNDS.....	304
XXX. DYES AND STAINS.....	314
XXXI. TERPENES AND RELATED SUBSTANCES.....	328
XXXII. VEGETABLE ALKALOIDS.....	335
XXXIII. ARSENIC AND MERCURY COMPOUNDS OF THE AROMATIC SERIES.	338
XXXIV. A BRIEF OUTLINE FOR THE IDENTIFICATION OF ORGANIC COMPOUNDS.....	344

## GENERAL TOPICS

XXXV. PLANT AND ANIMAL PIGMENTS: CHLOROPHYLL, CAROTIN, XANTHOPHYLL, FLAVONES, ANTHOCYANINS, HEMOGLOBIN AND BILE PIGMENTS.....	353
XXXVI. ENZYMES, VITAMINS AND HORMONES.....	357
XXXVII. SYSTEMATIC NOMENCLATURE OF ORGANIC COMPOUNDS .....	363

## APPENDIX

GLOSSARY.....	379
BOILING AND MELTING POINTS OF A NUMBER OF ORGANIC COMPOUNDS.	382
GENERAL REFERENCE BOOKS.....	385
INDEX.....	399

## NOTES FOR STUDENT

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REMEMBER that the laws in chemistry hold for organic as well as for inorganic chemistry. Correlate as many of the new facts with facts with which you are already familiar from your previous studies.

Classification in organic chemistry has been carried to an exceptional degree. One type reaction often gives the key to hundreds of individual reactions. Emphasize, therefore, type formulas and type reactions and make constant use of paper and pencil to practice the writing of formulas and equations.

To broaden your outlook, consult as frequently as possible the reading references given at the end of chapters.

Periodically refer to the "Replacement of Elements and Groups" on the next page.

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How can resourcefulness be acquired? Do it by pumping into a man information? No, not at all. There is only one thing which will really train the human mind, and that is the voluntary use of the mind by the man himself. You may aid him, you may guide him, you may suggest to him, and, above all, you may inspire him; but the only thing that is worth having is that which he gets by his own exertions, and what he gets is proportionate to the effort he puts into it. It is the voluntary exercise of his own mind, and I care very little about what he exercises it upon.—  
A. LAWRENCE LOWELL.



# AN INTRODUCTION TO ORGANIC CHEMISTRY

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## CHAPTER I INTRODUCTION

LONG ago man conceived the idea that between the living and the lifeless there is a sharp dividing line. A careful study of the colors of the spectrum, or a consideration of evolutionary problems, might have made him reconsider this view. It would have been more logical to assume that we probably cannot tell just where the "lifeless" ends and the "living" begins. That, indeed, is the modern point of view.

Even as late as a century ago, chemists still had faith in the classification of chemical compounds into "organic" or "inorganic," the "organic" being distinguished from the "inorganic" on the supposition that the former had some kind of "vital" or "life force," which made it seem quite impossible that a chemist could ever hope to reproduce an "organic" substance in the laboratory. (Formerly substances of mineral origin were classed as "inorganic"; those of animal or vegetable origin were classed as "organic.")

These notions of "organic" and "inorganic" were rudely shaken by the work of Wöhler, a distinguished German chemist, who, in 1828, succeeded in preparing urea in his laboratory by heating ammonium cyanate (p. 119),  $\text{[KCNO + (NH}_4\text{)}_2\text{SO}_4\text{]}$ . Now if any one compound can be called "organic," such a distinction certainly belongs to urea, for it is the chief end product of the decomposition of proteins in the body and is the principal nitrogenous constituent of the urine.

This epoch-making work of Wöhler's was not, as is generally supposed, at once accepted unconditionally. Sometimes the scientist does not take to scientific changes any more quickly than

does the average citizen to social or political changes. But in time other examples of the production of "organic" substances in the chemist's laboratory were recorded, and the old idea became less and less important. Chemists prepared or synthesized acetic acid, fats, alcohol, oxalic acid, mustard oil, oil of bitter almonds, sugars, camphor, uric acid, indigo, adrenaline, protein-like substances and thousands of others, more or less complex—all, however, typically "organic" substances. And we are far from having reached the limit. It is conceivable that in the not distant future some of the food we use will be made in the chemist's laboratory. Many are of the opinion that a judicious combination of the work of the physical chemist and the organic chemist will result, eventually, in solving the riddle of life itself.

We still retain the words "organic" and "inorganic," though we no longer think of them in the time-honored sense. What we call "**organic**" **chemistry** may more aptly be called the **chemistry of the carbon compounds**, for that is just what "organic" chemistry deals with.

But in reality we do not draw the line too sharply. Such compounds as carbon dioxide, carbon monoxide, carbon disulfide, hydrogen cyanide and the carbonates are usually included in texts on inorganic chemistry, though, of course, they are carbon compounds, and according to the definition should be included under "organic" chemistry.

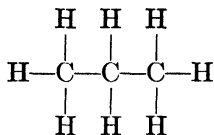
The fundamental laws of chemistry, which the student has taken up in his inorganic chemistry course, apply to organic chemistry with equal or perhaps greater force. If, then, the dividing line between "organic" and "inorganic" chemistry is not a sharp one, why the necessity for having these two subdivisions? We shall enumerate a number of reasons.

1. The number of compounds of carbon known to-day exceed 225,000, and the number of compounds which do not contain carbon are only about 26,000.

2. In general, organic and inorganic compounds show marked differences in solubility, the former being usually soluble in ether, alcohol, chloroform, benzene, etc., while the latter are not; whereas many of the inorganic compounds are soluble in water and the organic ones are not.

3. The atoms of carbon have the unique property of combining with one another to form chain-like structures—a property not frequently shown by other elements: for example,





4. Organic compounds are, as a rule, less stable than inorganic; they are much more easily susceptible to chemical and physical changes. (Organic compounds are decomposed at relatively low temperatures.)

5. "Type" reactions are quite frequent in organic chemistry. For example, there are hundreds of organic compounds which react with nitric acid to form "nitro" compounds (p. 231), hundreds of which react with reducing agents to yield "amino" compounds, etc.

6. There is often a marked difference in the velocity of reaction. The change of one organic compound to another is usually a relatively slow process, whereas the transformation of inorganic substances is often practically instantaneous.

7. Reactions in organic chemistry are, as a rule, mostly non-ionic, the solutions being non-conductors of electricity; whereas, reactions in inorganic chemistry are largely ionic. This explains, for example, why, when solutions of sodium chloride and silver nitrate are mixed, an immediate precipitate of silver chloride is obtained, whereas, we get no precipitate upon mixing solutions of pure carbon tetrachloride ( $\text{CCl}_4$ ) and silver nitrate. Organic acids, bases and salts ionize.

8. Reactions in organic chemistry often tend to become quite complex, and there are possibilities of many "side" or "secondary" reactions (p. 227).

9. The complexity in structure exhibited by some organic compounds is quite unknown among inorganic compounds (p. 319).

10. Organic compounds often show a property called "isomerism" which we shall discuss later in some detail (p. 21), but this phenomenon is very little known in inorganic chemistry. For example, when we write  $\text{HNO}_3$  we have reference to nitric acid, and to nitric acid alone, but when we write  $\text{C}_2\text{H}_6\text{O}$  this may stand for ethyl alcohol or for methyl ether, and the only way we can distinguish the one from the other is by writing graphic or structural formulas (p. 21), which give some idea of the arrangement of the atoms within the molecule. That is the reason why graphic and structural formulas are used so extensively in organic chemistry (pp. 14, 279).

**Importance and Applications.**—We have already mentioned the fact that more than 225,000 compounds are grouped under organic chemistry. Many of these find various applications in our daily life. Some of them are so common that merely mentioning their names will suggest to the student many of their applications. Picking a few of these substances more or less at random, we may refer to starch, sugar, fats, oils, proteins, paper, rayon, soap, explosives, photographic developers, bakelite, anesthetics, disinfectants, antiseptics, dyes, drugs, waxes, ether, natural gas, perfumes, glue, citric acid, alcohol, saccharin, artificial food colors, caffeine, cellulose, camphor, rubber, flavoring essences, gasoline, vaseline, coal tar, glycerine, aniline, indigo, salvarsan, lacquer industry (duco, etc.), etc. And it may be added that the various transformations which the foodstuffs and cellular tissue undergo in the plant and animal kingdom, involving complex syntheses and decompositions, are essentially those which can best be studied by the organic chemist.

**Other Sciences Based on Organic Chemistry.**—Physiological (or Bio-) chemistry (which deals with the chemical processes that take place in animals and plants), food chemistry, and organic analysis, all have their basis in organic chemistry. Various aspects of medicine, dentistry and pharmacy require training in organic chemistry. We shall illustrate this interdependence with a few examples.

A problem of general importance in bacteriology is to find some substance which has the property of destroying a certain type of bacteria without at the same time injuring the body tissues. Ehrlich, the German physician, who was also a trained chemist, found a cure for syphilis by the use of arsphenamine (p. 339) (also called salvarsan and "606"), which he synthesized in the laboratory. More recently the work of Jacobs and Heidelberger at the Rockefeller Institute, N. Y., on the application of various arsenical compounds to medicine, holds out hope that one of these will prove of distinct value in the treatment of sleeping sickness. Mention may also be made of the use of "chloramine-T" (p. 282) and other organic compounds containing chlorine, in the treatment of infected wounds. During the war, Dakin and Carrel found that "chloramine-T," given under certain conditions, is strong enough to destroy micro-organisms, without at the same time harming the tissues.

Another problem, this time of particular importance to physi-

ologists and general medical practitioners, is the isolation, in a chemically pure state, of the active principles of glands in the body. One of the active principles of the adrenal glands, adrenaline (or, as it is sometimes called, "epinephrine") has not only been isolated from the gland, but has actually been synthesized in the laboratory. In this work Abel of Johns Hopkins and the late Takamine, a Japanese chemist who had established himself in the United States, took leading parts. Lately, the active principle of the thyroid gland, thyroxin, has been isolated by Kendall of the Mayo Clinic in Rochester, Minn., and Harington has also succeeded in synthesizing it. And we may mention that insulin, ("iletin") an active principle of the pancreas, which has been shown by the Canadian, Banting, to play such an important rôle in diabetes, has lately been obtained in a crystalline form by Abel.

Cocaine, novocaine, butyn, benzyl alcohol, benzyl benzoate and ethylene as anesthetics; hexyl resorcinol, dibromin as antiseptics; mercurochrome-220 as a germicide; the essential constituents of chaulmoogra oil in the treatment of leprosy; caffeine and related substances as diuretics; barbital (veronal), allonal and luminal as hypnotics; thymol and carbon tetrachloride as a cure for hookworm; the relation of ergosterol and vitamin D and the relation of vitamin E to the problem of reproduction; the isolation and the ultimate synthesis of glutathione, a cell constituent related to body oxidation; and the extraction of the active principle of the parathyroid gland are only a few illustrations of the comparatively recent developments in the application of organic chemistry to medicine.

At so rapid a rate is progress in this field, that, in the last few years, several noteworthy discoveries have been made. For example, sucrose has been made in the chemist's laboratory (p. 179); a new form of synthetic rubber has been announced (p. 40); hematin, the important component of hemoglobin, has been synthesized; carotin, a hydrocarbon, is apparently the forerunner of vitamin A; a liver extract cures pernicious anemia; and active extracts of hormones from the reproductive glands, from the adrenals and from the pituitary have been obtained.

**Sources of Organic Substances.**—A. Organic compounds may be traced either to the plant or animal kingdom. Out of carbon dioxide, water, and various constituents from the soil, in the presence of light, the plant builds a veritable galaxy of substances: sugars, starches, cellulose, alkaloids (morphine in opium—

nicotine in tobacco), acids (citric and tartaric), salts ("tartar" in grapes), esters (flavoring substances of fruits), essential oils (peppermint, lemon), camphor, vegetable oils (linseed, cottonseed, olive), herbs (from which drugs are made and which were so largely used in days gone by), gum arabic, flavoring substances (vanilla), dyes (indigo, logwood, fustic), perfumes, tannin (from nutgalls), etc.

*B. Plants and animals* furnish us with fats, proteins, carbohydrates, enzymes and vitamins, and we often go to the animal kingdom for a number of products, such as urea, uric acid, gelatin, toxins and antitoxins.

*C. Destructive Distillation of Coal.*—When soft coal is strongly heated in a retort, this complex substance breaks down into a number of (chemically) simpler substances. The conversion of a complex substance into a number of simpler substances by the aid of heat (in the absence of air) is known as "destructive distillation." The destructive distillation of coal yields coal gas (illuminating gas), ammonia, coke and coal tar. Coal tar, at one time discarded as a useless by-product, is now the starting-point for any number of organic products (some 225 compounds have been so far isolated). Out of coal tar we get benzene, toluene, naphthalene, anthracene, carbolic acid, the cresols, etc.; and these substances (the source of many aromatic compounds, see p. 211), in turn, yield thousands of other organic compounds, many of them of great value as dyes, perfumes, drugs, etc. (see chart, p. 211). Perkin, an Englishman, was the first (in 1856) to prepare a coal-tar dye, but the development of the dye industry is due largely to the Germans, who, prior to the late war, were responsible for much research work in this field. Post-war developments in this country and in England have already reached such a stage as to ensure the establishment of permanent dye and other related industries.

*D. Destructive Distillation of Wood.*—The important products obtained from wood are acetic acid, methanol (wood alcohol), acetone, (indirectly), wood tar, combustible gases and charcoal.

*E. Destructive Distillation of Bones.*—This yields animal charcoal (bone black) and bone oil, out of the latter of which a number of nitrogenous compounds, characterized by their disagreeable odor, are obtained (pyridine and quinoline are examples).

*F. Fractional Distillation of Petroleum.*—A mixture of two or more liquids having different boiling-points may usually be sepa-

rated from one another by a process of distillation, the liquid with the lower boiling-point distilling over first. A process which separates two or more liquids by making use of their different boiling-points is called "fractional distillation." The fractional distillation of petroleum yields a number of important commercial products, such as naphtha, gasoline, kerosene, gas oil, lubricating oil, cylinder oil, vaseline, etc.

*G. Natural Gas.*—Within the past few years there have been important new developments due to the production of compounds of practical importance from natural gas. Many of these new compounds have been synthesized from ethylene as the starting material. (See chart facing p. 142.) ✓

*H. Fermentation.*—It was for a long time supposed that in the conversion of sugar into alcohol by means of yeast, the living cells of the latter were primarily responsible for the change. We now know that what brings about this change is not the cells themselves, but substances produced by the cells, known as "enzymes." Changes analogous to the conversion of sugar into alcohol are known as "fermentation." The sweet apple juice turns to cider (due to the formation of alcohol), and finally to cider vinegar (due to the oxidation of the alcohol into acetic acid). Milk on standing, or when "inoculated" with bacteria, becomes sour, due to the conversion of lactose (milk sugar) into lactic acid.

*I. Putrefaction.*—Putrefaction may be defined as the decomposition of animal or vegetable substances brought about largely by micro-organisms, resulting in diverse products, some of which have a foul odor. Among the products of putrefaction are amines, fatty acids, ammonia and its compounds,  $\text{H}_2\text{S}$ , methane, etc.

**Purification of Organic Compounds.**—Most of the organic compounds when first prepared are impure. Before the physical constants and chemical analyses (qualitative and quantitative) of a compound can be determined, it must be obtained in a pure state. For details of the methods used in the preparation of chemically pure substances, we must refer the student to appropriate laboratory texts (see p. 386), and only the barest outline will be given here.

The substance as first prepared is generally in an impure state. It may be purified by one or more of several processes, such as crystallization, distillation, sublimation, extraction, dialysis, precipitation, decolorization (for details refer to laboratory manuals quoted). Almost all pure organic compounds have a definite

melting-point (m.p.), or boiling-point (b.p.), or both. The melting- or boiling-point of the compound is, therefore, determined after the preliminary process of purification. A definite m.p. or b.p. is an important criterion of purity; in addition, the specific gravity, solubility, crystalline structure, refractive index, optical activity, etc., are also made use of. (The principles involved, as well as the details of manipulation, will become familiar to the student as a result of his laboratory work.) Having obtained the pure product, the next step is an analysis of the compound.

**Elements Present in Organic Compounds.**—Numerous as the compounds of carbon are, most of them contain but two to five different elements in the molecule. There are hundreds of compounds which contain merely the elements carbon and hydrogen. These are known as hydrocarbons. Methane ( $\text{CH}_4$ ), benzene ( $\text{C}_6\text{H}_6$ ), naphthalene ( $\text{C}_{10}\text{H}_8$ ) and anthracene ( $\text{C}_{14}\text{H}_{10}$ ), are examples. Many contain the element oxygen in addition to carbon and hydrogen; as for example, the sugars, fats, starches, alcohols, ethers, acetic acid and glycerol. Many are composed of carbon, hydrogen and nitrogen, as hydrocyanic acid and aniline. Examples of compounds containing carbon, hydrogen, oxygen and nitrogen are some of the alkaloids, proteins, indigo and urea; and those containing carbon, hydrogen and a halogen are chloroform and iodoform.

Often, in addition to the elements already mentioned, we find sulfur and phosphorus. Many of the proteins contain appreciable quantities of the former element, and the phosphatides, such as lecithin and cephalin, which are important cellular constituents, contain phosphorus. (Hopkins has isolated a substance from cells, to which he has given the name "glutathione," which contains sulfur and which is regarded as a substance that plays a very important rôle in all cellular oxidations. Quite recently he has synthesized this substance.)

Elements in addition to those already mentioned are often met with. Following the pioneer work of Ehrlich on salvarsan, very many organic compounds of arsenic, antimony, bismuth and mercury have been prepared. Quite recently an organic compound of lead, lead tetraethyl, has been used to prevent "knocking" in automobiles (p. 199). Many salts of organic acids, such as those of sodium, potassium, calcium, etc., are found in nature or may be prepared in the laboratory.

**Analysis of Organic Compounds.**—(Detailed directions are given in laboratory manuals.)<sup>1</sup> Before a quantitative analysis of a compound is made, a qualitative analysis, involving the detection of the elements present, is undertaken. In the course of the qualitative analysis, carbon in most organic compounds may be detected by heating the compound with copper oxide, the carbon thereby being oxidized to carbon dioxide, the presence of which may be shown with lime water. The same process oxidizes any hydrogen present to water, which is usually seen to collect in the upper (cooler) part of the tube. Nitrogen may be detected either by heating the substance with soda lime ( $\text{NaOH} + \text{CaO}$ ), thereby converting the nitrogen into ammonia, or by fusion with sodium, whereby sodium cyanide is formed ( $\text{Na} + \text{C}$  of organic compound  $+ \text{N}$ ), which is then converted into ferrocyanide by heating with a ferrous salt, and ultimately to "prussian blue" by the addition of a ferric salt. Halogens may be recognized by heating the compound with copper oxide in a non-luminous flame, whereby a green coloration is obtained, due to the volatilization of the copper halide, or by making use of the sodium fusion test, whereby the halogen is converted into the corresponding sodium salt, which may then be tested with silver nitrate. (Remember that the halogen in organic combinations is mainly in a non-ionizable form, and therefore does not react with a solution of silver nitrate prior to its decomposition.)

If sulfur is present it may be recognized by fusion with sodium, whereby sodium sulfide is formed, and a solution of this compound when placed on a silver coin forms silver sulfide (brownish-black).

Phosphorus and any of the other elements (such as the metals) are detected just as in inorganic analysis. The test for phosphorus requires a preliminary fusion with an oxidizing mixture (such as potassium nitrate and sodium carbonate).

We have no satisfactory test for oxygen.

Many of the qualitative tests serve as the basis for the quantitative determinations. The carbon dioxide and water formed by the oxidation of a compound containing carbon and hydrogen

<sup>1</sup> Benedict, *Elementary Organic Analysis*; Cohen, *Laboratory Manual of Organic Chemistry*; Fisher, *Laboratory Manual of Organic Chemistry*; Gattermann, *Practical Methods of Organic Chemistry*; Kingscott and Knight, *Methods of Quantitative Organic Analysis*; Mulliken, *Identification of Pure Organic Compounds*; Price and Twiss, *A Course of Practical Organic Chemistry*; Pregl, *Quantitative Organic Microanalysis*; Sudborough and James, *Practical Organic Chemistry*.

are collected and weighed, and from the amounts of the products formed, the percentages of carbon and hydrogen in the original compound are calculated. The nitrogen in a compound may either be determined by the "Kjeldahl" method, whereby the element is converted into ammonia, or by the "Dumas" absolute method, whereby nitrogen gas is set free and its volume measured.

In the determination of the halogens, the compound is either oxidized with fuming nitric acid in presence of silver nitrate, the resulting silver halide weighed and the halogen calculated; or the compound is heated with pure calcium oxide, and the halogen in the resulting calcium halide determined either by precipitation or titration with silver nitrate.

Sulfur in an organic compound is determined by heating with fuming nitric acid, thereby converting it to sulfuric acid. This is then precipitated as barium sulfate with barium chloride. The percentage of sulfur is calculated from the weight of barium sulfate.

For estimating phosphorus and other elements, the methods outlined in inorganic quantitative analysis are followed.

Neither in its detection nor in its determination is there a good method available for oxygen when present in an organic compound. The general procedure is to determine the percentage of all the other elements present in the compound, subtract the total from 100, and "call" the difference the per cent of oxygen.

The principles underlying the analytical methods are quite simple, but the details for the quantitative determination of C, H, N and the other elements, are rather complex.

Experimental details have been worked out to determine percentages of elements even when as small a quantity as .002-.003 gram of a compound is available.<sup>1</sup>

The analysis just discussed is what is known as "ultimate" or "elementary" analysis. It refers to the percentage of the elements present in the compound. There is still another type of analysis, known as "proximate," with which the clinical, pharmaceutical or food chemist has much to do. This "proximate" organic analysis deals with the determination of ingredients present in a mixture, such as the fat or protein in milk, or the various nitrogenous constituents and sugar in urine, or the percentage of alcohol in wine, etc.

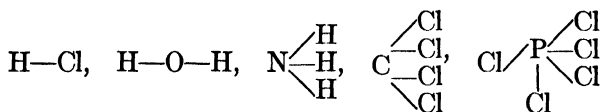
The quantitative analysis enables us to arrive at what is known

<sup>1</sup> Pregl, Quantitative Organic Microanalysis.



as the "empirical" or "simplest" formula; but this may not necessarily prove to be the "true" or "molecular" formula. For example, a quantitative analysis of acetylene and benzene would yield the same "empirical" formulas for both, namely,  $\text{CH}$ ; yet acetylene is written  $\text{C}_2\text{H}_2$  and benzene  $\text{C}_6\text{H}_6$ . In order to arrive at the actual or "molecular" formula, whether  $\text{C}_2\text{H}_2$  or  $\text{C}_6\text{H}_6$ , we must further proceed to a molecular weight determination, based on vapor density, or boiling-point, or freezing-point, etc. Here again the reader is referred to laboratory manuals or to books on physical chemistry for further details.<sup>1</sup>

**Valence and Structure in Inorganic Chemistry.**—Our studies in inorganic chemistry have led us to define valence as the number of atoms of hydrogen with which one atom of an element combines or replaces. To show such relationships graphically in any compound, we indicate valencies by lines or "bonds," each line representing one valency. Thus:



where not only are hydrogen, oxygen, nitrogen, carbon and phosphorus shown to be mono-, di-, tri-, tetra- and pentavalent elements, respectively, but these valencies are indicated by bonds, each bond representing one valency.

In organic chemistry, the use of graphic formulas is very extensive indeed, for only by some such method can the distinguishing features of a compound be brought out at a glance.

The difficulties that confront us may be seen from the following example, which has already been touched upon once before.  $\text{HNO}_3$  is the formula for nitric acid and for this compound alone, but  $\text{C}_2\text{H}_6\text{O}$  stands for grain alcohol or methyl ether, and  $\text{C}_4\text{H}_{10}$  may represent two different compounds. Although the molecular formulas are the same, the physical and chemical properties are more or less different. We say that in these cases the different compounds are due to differences in the internal structure of the

<sup>1</sup> Findlay, Practical Physical Chemistry; Getman, Laboratory Exercises in Physical Chemistry; Gray, Manual of Practical Physical Chemistry.

molecule, and our graphic formulas, which we shall use so much, attempt to give us a picture of such differences. Of course, these graphic formulas do not, and cannot represent the actual differences of any two compounds, or for that matter the actual structure of any one compound. Matter, to begin with, has three, not two, dimensions in space, and no structure drawn on paper can truly represent actual conditions. Nevertheless, these two-dimensional formulas have proved of inestimable value in clearing up many difficulties, as the student will appreciate when he proceeds to the various chapters.

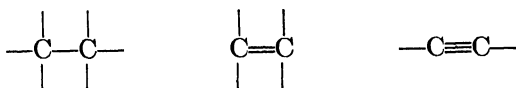
**The Fundamental Bases underlying the Structural Theory of Organic Chemistry:**

1. The valence of carbon, almost without exception, is four,<sup>1</sup> and is represented as

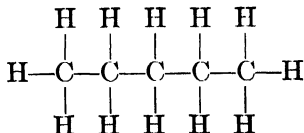


where any one bond bears exactly the same relationship to the carbon atom as any other bond. These valencies may be represented as directed toward the corners of a regular tetrahedron, constructed around the carbon atom as a center, and are, therefore, equidistant from each other in space.

2. Carbon atoms may be united either by single, double or triple bonds:



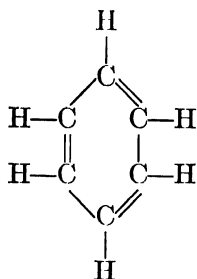
3. Carbon atoms may form a "straight" or "open" chain; for example,



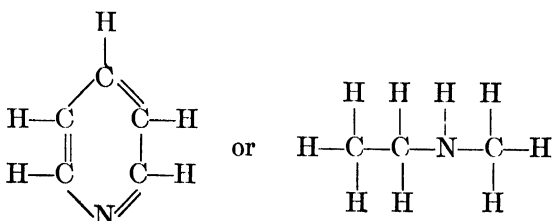
<sup>1</sup> There are several striking exceptions, however, such as CO (p. 163), C=NOH (p. 164), R—N=C (p. 162), and (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>C (p. 218).

<sup>2</sup> It is suggested that at this point the instructor illustrate by means of models the probable spatial arrangement (in the form of a regular tetrahedron) of the methane molecule.

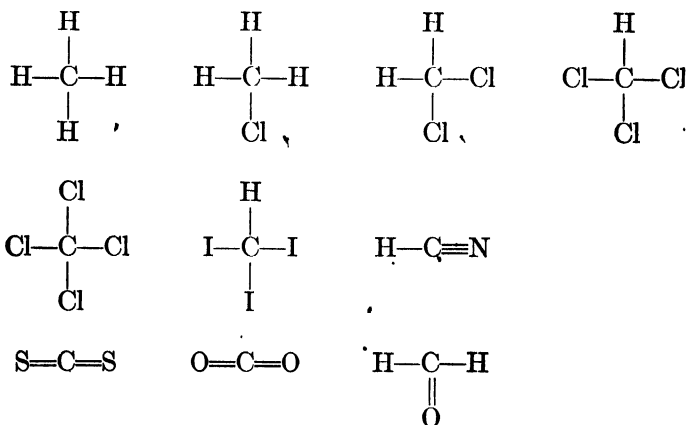
4. Carbon atoms may form a "closed" chain; for example,



5. Other elements besides carbon may enter a carbon chain, or a ring: e.g.,



6. Elements may substitute one another in compounds; that is, one element in a compound may be removed, and another may take its place; for example,

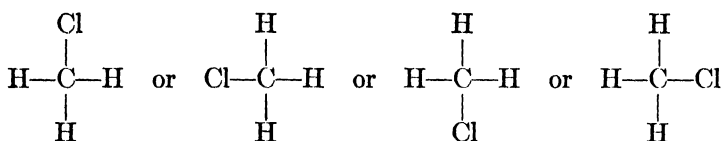


It must not be supposed that when we write methane,

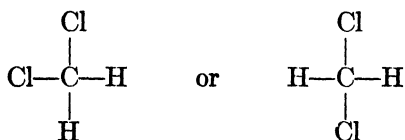
$$\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H} \end{array}$$

we have any intention of fixing the atoms in space.

In any case—and this has already been referred to—two-dimensional configurations cannot truly represent the structure of any form of matter. But we do wish to emphasize that in the formula for methane the four hydrogen atoms are to be regarded as of equal value, so that when a hydrogen atom is replaced by a chlorine atom, it does not matter whether we write



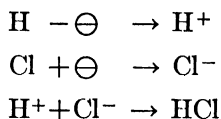
for they all represent one and the same compound, namely, monochloromethane; nor, if two hydrogen atoms are replaced by two chlorine atoms, does it matter whether we write



for both represent the same compound, dichloromethane.

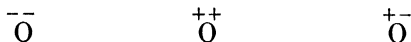
**The Electron Conception of Valence.**—Based on modern work on the structure of the atom, many chemists have been busy recently developing ideas of valency in accord with the electronic conceptions of matter. As early as 1907 J. J. Thomson stated that for each valency bond established between two atoms, the transference of one—negatively charged—corpuscle (electron) from one atom to the other has taken place, the atom receiving the corpuscle (electron) acquiring a unit negative charge, while the atom losing the electron acquires a unit positive charge. Thus, a neutral H atom and a neutral Cl atom would become positively and

negatively charged, respectively, should the H atom lose an electron to the Cl atom:



An atom is capable of losing or gaining as many electrons as it has valencies and may function either as a positively or negatively charged atom. (Most elements have a greater tendency to behave one way than another.) If the Cl atom loses an electron, it becomes positively charged; e.g., hypochlorous acid,  $\overset{+}{\text{Cl}} \overset{-}{\text{O}} \overset{+}{\text{H}}$ ; but if it gains an electron, it becomes negatively charged; e.g.,  $\overset{+}{\text{H}} \overset{-}{\text{Cl}}$ .

A divalent atom may function in three ways: through the gain of two electrons; through the loss of two electrons; and through the simultaneous loss of one electron and gain of another; e.g.,

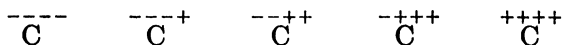


With a trivalent element there are four possibilities:

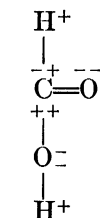
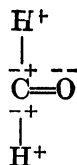
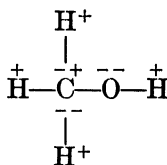
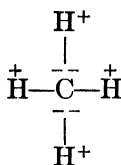


An atom, then, whose valence is  $n$  may function electronically in  $n+1$  different ways.

If this conception be applied to carbon, we might expect the carbon atom, with its tetravalency, to function in five different ways:



Applying the electronic conception of valence to a few simple carbon compounds—to methane, methanol (wood alcohol), formaldehyde, formic acid and carbon dioxide—we get the following:



(Consult the references at the end of the chapter—Falk and Nelson, Noyes and Langmuir.)

**Classification of Organic Compounds.**—There are two main divisions, the “**aliphatic**” and the “**aromatic**.”

The aliphatic compounds are related to methane, CH<sub>4</sub>, and are “open chain.” They get their name from the fact that animal and vegetable fats belong to this series.

The aromatic (“ring” or “cyclic”) compounds are related to benzene, C<sub>6</sub>H<sub>6</sub>, and many are characterized by fragrant odors; hence the name.

The line of demarcation of aliphatic and aromatic compounds is not a sharp one, for not all aliphatic compounds can be directly traced to fatty substances, nor do all aromatic compounds have odors. On the other hand, many aliphatic compounds possess very characteristic odors. Nevertheless, there are, as a rule, some general differences which help to differentiate the two great divisions, perhaps the most important being differences in a number of chemical properties (p. 213).

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## CHAPTER II

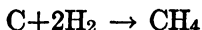
### SATURATED HYDROCARBONS OR PARAFFINS AND PETROLEUM

As its name implies, a hydrocarbon is a compound containing hydrogen and carbon.

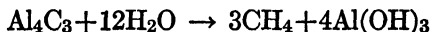
**Methane**,  $\text{CH}_4$ , is the simplest compound of the hydrocarbon group.

**Occurrence.**—The decomposition of vegetable and animal matter gives rise to this gas. One of the gases arising from marshes is methane, hence its name "marsh gas." It is also one of the gases produced in intestinal putrefaction. It forms a large percentage of the constituents found in natural gas (80 per cent and above) and coal gas (30–40 per cent). Fires and explosions in coal mines are mainly due to the ignition of mixtures of methane and air; hence methane is also known as "fire-damp."

**Preparation.**—Methane may be synthesized from its elements by passing hydrogen over carbon in presence of nickel (catalyst) at  $475^\circ$ .

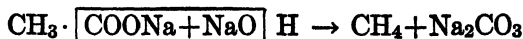


It may also be obtained by the action of water on certain carbides, such as aluminum carbide:



This reaction is of interest since it led Moissan, the French chemist, to speculate on the origin of natural gas. He held this to be due to the action of water on various metallic carbides. (It must be remembered that methane is not always the product formed when water acts on a carbide. The student will recall that water acts on calcium carbide, for example, to give acetylene.)

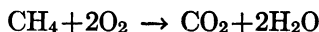
The laboratory method depends upon heating a mixture of fused sodium acetate and soda lime ( $\text{NaOH} + \text{CaO}$ ):





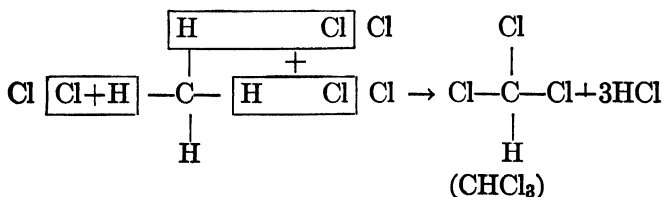
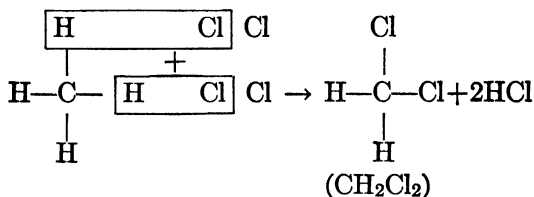
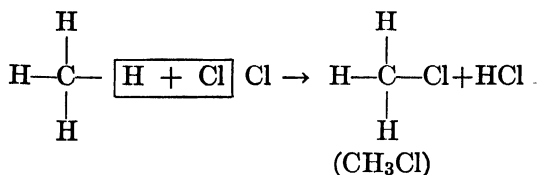
(The sodium acetate is the sodium salt of acetic acid,  $\text{CH}_3 \cdot \text{COOH}$ . The latter, in turn, may be regarded as methane,  $\text{CH}_4$ , having one of its hydrogens replaced by the  $\text{COOH}$  group, known as the "carboxyl" group. See p. 85.)

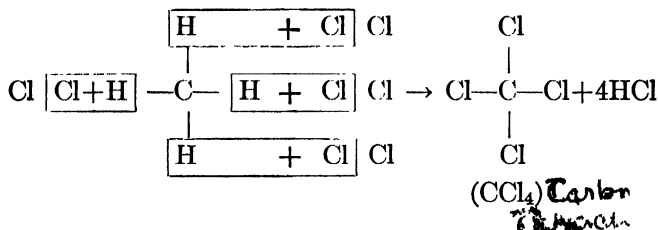
**Properties.**—It is a colorless gas with a slight odor, and burns with an almost non-luminous flame:



Methane has high fuel value. If mixed with air and ignited, it explodes; this explains many explosions in coal mines ("fire-damp").

The chemical properties of methane apply to the entire group of saturated hydrocarbons (p. 26) of which methane is the first member. Methane is an inactive and stable compound. (Methane and other hydrocarbons of this series are known as paraffins, which means "little affinity.") The common reagents, such as hydrochloric, nitric, sulfuric and chromic acids, and sodium and potassium hydroxides, do not react with it. On the other hand, the halogens, such as chlorine and bromine, react rather vigorously with methane, particularly in the presence of sunlight:





You will notice, in these examples, that the chlorine replaces the hydrogen in the molecule. Whenever an element or a group of elements replaces another element or group of elements in a compound, the process is known as "substitution." Such reactions are characteristic of saturated hydrocarbons.  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$  are chlorine substitution products of methane.

$\text{CH}_3\text{Cl}$  = methyl chloride or monochloromethane;  
 ( $\text{CH}_3$  = methyl group) (monovalent).

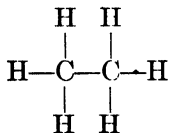
$\text{CH}_2\text{Cl}_2$  = methylene chloride or dichloromethane;  
 ( $\text{CH}_2$  = methylene group) (divalent);

$\text{CHCl}_3$  = trichloromethane or chloroform.

$\text{CCl}_4$  = tetrachloromethane or carbon tetrachloride.

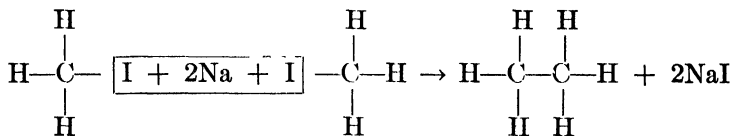
(Many of these names need not be memorized. If the student will but remember that these compounds are substitution products of methane, he will have little difficulty in naming them. In  $\text{CH}_3\text{Cl}$ , for example, the compound may logically be regarded as methane in which one of the hydrogen atoms has been replaced by chlorine; hence the name "monochloromethane." But it must also be remembered that the  $\text{CH}_3$  group is known as a "methyl" group; hence also the name "methyl chloride.")

**Ethane**,  $\text{C}_2\text{H}_6$ . This is the second member of the paraffin series, and in its general physical and chemical properties shows resemblances to methane. It is found in natural gas and petroleum and is separated by fractional distillation from other hydrocarbons. Its formula is represented by



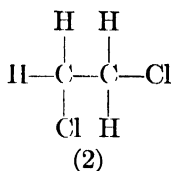
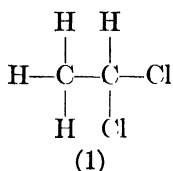
and it differs from methane by  $\text{CH}_2$ . It may be regarded as methane in which one of the hydrogens is replaced by a  $\text{CH}_3$  group; that is,  $\text{CH}_3 \cdot \text{CH}_3$ , methyl methane, or dimethyl.

Further light on the structure of ethane is shed by the way in which it can be synthesized. Methyl iodide reacts with sodium in the following way (*Wurtz synthesis*):



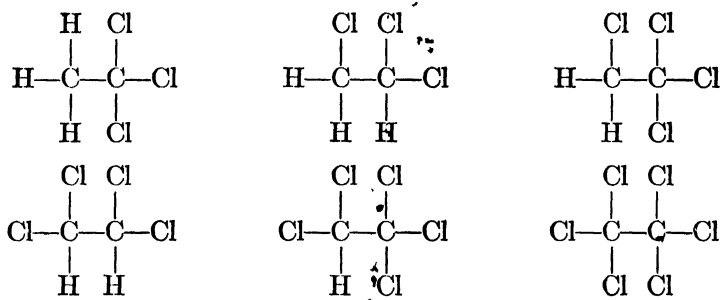
In other words, the formation of ethane is here shown to be a coupling of two methyl groups.

**Isomerism.**—Experience has shown that only one mono-substitution product of ethane can be obtained, but it is possible to obtain two di-substitution products, both having the same molecular formula,  $\text{C}_2\text{H}_4\text{Cl}_2$ , but differing from one another in physical and chemical properties. Here we clearly have a case of isomerism, and the graphic formulas bear this out:

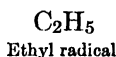
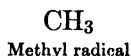


for in (1) we see two chlorine atoms attached to the same carbon atom, and in (2) the two chlorine atoms are attached to two different carbon atoms. Whenever we have two or more compounds having the same molecular formula, but differing in physical and chemical properties, we have an example of isomerism, and the individual compounds are known as isomers. (Let us illustrate this question of isomerism with an analogy. Suppose we take the figures 4, 7, 5. It obviously makes very much of a difference as to whether we write 475 or 754 or 547 or 745 or 574 or 457. Yet all we have done is to *rearrange* the figures; and by merely *rearranging* the numerals we have obtained *totally different* sums. So it may be with two compounds such as are illustrated above: they may have the same empirical formulas, yet be quite different substances because of the different *arrangement* of the atoms within the molecule.)

Experience has also shown that there are but two tri-, two tetra-, one penta-, and one hexa- substitution products of ethane; and the student can confirm this by studying the graphic formulas:



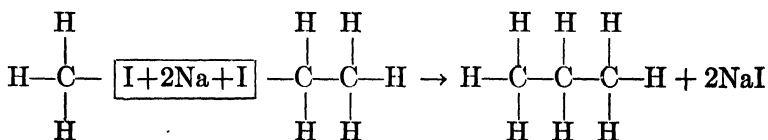
In naming substitution products of ethane, the system adopted for methane is used:



$\text{C}_2\text{H}_5\text{I}$ , for example, is ethyl iodide, or iodoethane, and  $\text{C}_2\text{H}_5\text{OH}$  is ethyl hydroxide, or hydroxyethane.

(The name for the radical corresponding to the hydrocarbon is obtained by changing the suffix *-ane* into *-yl*.)

**Propane**,  $\text{C}_3\text{H}_8$ .—We have seen that ethane,  $\text{C}_2\text{H}_6$ , may be regarded as methane,  $\text{CH}_4$ , to which  $\text{CH}_2$  has been added. Similarly, propane,  $\text{C}_3\text{H}_8$ , may be regarded as ethane,  $\text{C}_2\text{H}_6$ , to which  $\text{CH}_2$  has been added; or as  $\text{C}_2\text{H}_5$  in which one of the hydrogens has been replaced by a  $\text{CH}_3$  group. Its structure becomes evident by examining its synthetic method of preparation. Ethyl iodide and methyl iodide react in the presence of sodium to form propane. The principle was made use of in the synthesis of ethane, and may be made use of in the synthesis of other hydrocarbons.

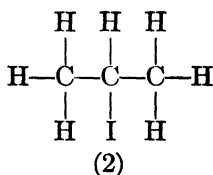
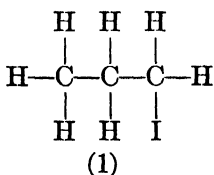


In this reaction ethane and butane,  $\text{C}_4\text{H}_{10}$ , are also produced. (Why?)

(Why may propane be called ethylmethane, or dimethylmethane, or methylethane, or methyl ethyl?)

(If  $C_3H_8$  is propane, what would its radical,  $C_3H_7$ , be called?)

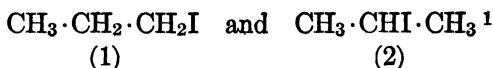
We pointed out that in ethane we have but one mono-substitution product and two di-substitution products, and we saw how the graphic formulas helped to explain these facts. When we come to propane, we find that two mono-substitution products are possible, one differing from the other in physical and chemical properties. Here again the graphic formulas are helpful in explaining experimental facts:



for it will be seen that in (1) the iodine atom is attached to a carbon atom, which in turn is attached to two hydrogen and one carbon atoms, whereas in (2) the iodine atom is attached to a carbon atom which in turn is attached to two carbon and one hydrogen atoms.

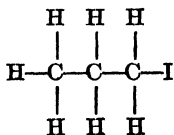
**Butanes,  $C_4H_{10}$ .**—Two butanes with this formula are known.

In the preceding paragraph we pointed out that there are two isomeric propyl iodides which, for convenience, we shall now write according to the "structural" or "constitutional" formulas.



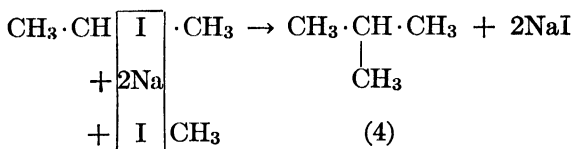
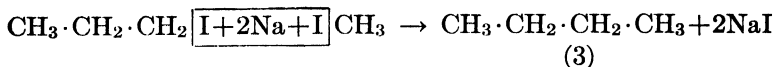
Now, it may be asked, what will happen if first (1) and then (2) are treated with methyl iodide in the presence of sodium? Are

<sup>1</sup> Periods are often used in place of bonds when writing structural or constitutional formulas, so that  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2\text{I}$  really means  $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{I}$ , which in turn indicates



As the student proceeds with his studies in organic chemistry, he will find it unnecessary to indicate either dots or dashes for at least some of the simpler types of compounds.

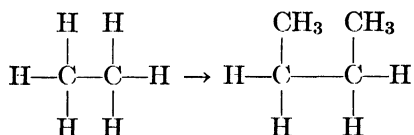
we going to get two identical compounds? This is hardly likely, since (1) and (2) are different. In reality, the two compounds obtained are different,—different in properties, but alike in having the same molecular formula,  $C_4H_{10}$ .



(3) and (4) are isomeric, (3) being known as normal ("straight-chain") or *n*-butane, and (4) as *iso*- ("branched-chain") butane.

(Why may normal butane be given any one of the following names: methylpropane, ethylethane, diethyl, propylmethane and symmetrical dimethylethane? Why may isobutane also be called trimethylmethane and unsymmetrical dimethylethane?)

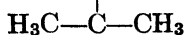
(If two of the hydrogens in ethane which are attached to two different carbon atoms are replaced by methyl groups, we get butane or symmetrical dimethylethane:



If, however, the two hydrogen atoms replaced by two methyl groups are on the same carbon atom, then we get isobutane, or unsymmetrical dimethylethane.)

Propane and the butanes are used for refrigerating purposes.

**Pentanes**,  $C_5H_{12}$ .—Three pentanes are known:

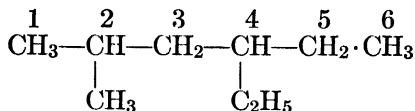


or

neopentane

(Give as many names to these compounds as you can.)

**Nomenclature of Saturated Hydrocarbons.**—Select the longest chain of carbon atoms in the molecule and number the carbon atoms. Consider the side chains as substituents. For example,



2-methyl-4-ethyl hexane.

The table on page 26 includes a few normal hydrocarbons and the corresponding monovalent radicals.

From the table we conclude the following:

1. Every hydrocarbon in this series is saturated (single bonds).
2. The name of each hydrocarbon ends in *ane*.
3. The hydrocarbons from  $\text{CH}_4$  to  $\text{C}_4\text{H}_{10}$  are gases, from  $\text{C}_5$  to  $\text{C}_{16}$ , liquids at ordinary temperatures, and from  $\text{C}_{17}$ , solids.
4. The melting- and boiling-points increase with the increase in molecular weight.
5. The difference between any two consecutive members in this series is  $\text{CH}_2$ .

(Whenever we have a series of compounds where the difference between any two consecutive members is  $\text{CH}_2$ , we get what is known as a **homologous** series. The word "homologue" signifies "a member of the series." Homologous series are frequently met with in organic chemistry, and we shall refer to them repeatedly. The great value in the study of these homologous series lies in the fact that members of such a series are really members of the same family, and, therefore, show strong family resemblances; or, to speak in terms of chemistry, strong chemical resemblances. This does not mean that the members of an homologous series are exactly alike chemically; but it does mean that they have certain common characteristics which distinguish them from other classes of compounds.)

6. Their type formula may be represented algebraically by  $\text{C}_n\text{H}_{2n+2}$ .

7. The names of the radicals end in "yl," the suffix "ane" of the hydrocarbon being changed to "yl" (methane  $\rightarrow$  methyl).

8. The type formula for radicals is  $\text{C}_n\text{H}_{2n+1}$  (monovalent.)

9. The paraffins are known as "alkanes"; hence the group is

## PARAFFIN SERIES \*

Formula	Name	Boiling-Point	Melting-Point	Name of Mono-valent Radical	Formula of Radical
$\text{CH}_4$	Methane	-164	-184	Methyl	$\text{CH}_3$
$\text{C}_2\text{H}_6$	Ethane	- 89.3	-172	Ethyl	$\text{C}_2\text{H}_5$
$\text{C}_3\text{H}_8$	Propane	- 44.1	....	Propyl	$\text{C}_3\text{H}_7$
$\text{C}_4\text{H}_{10}$	Butane	- 0.1	-135	Butyl	$\text{C}_4\text{H}_9$
$\text{C}_5\text{H}_{12}$	Pentane	+ 36.3	-130	Amyl or Pentyl	$\text{C}_5\text{H}_{11}$
$\text{C}_6\text{H}_{14}$	Hexane	+ 68.9	- 94	Hexyl	$\text{C}_6\text{H}_{13}$
$\text{C}_7\text{H}_{16}$	Heptane	+ 98.2	- 97	Heptyl	$\text{C}_7\text{H}_{15}$
$\text{C}_8\text{H}_{18}$	Octane	+125.8	- 56	Octyl	$\text{C}_8\text{H}_{17}$
$\text{C}_9\text{H}_{20}$	Nonane	+149.5	- 51	Nonyl	$\text{C}_9\text{H}_{19}$
$\text{C}_{10}\text{H}_{22}$	Decane	+173	- 32	Decyl	$\text{C}_{10}\text{H}_{21}$
$\text{C}_{11}\text{H}_{24}$	Undecane	+194.5	- 26.5	Undecyl	$\text{C}_{11}\text{H}_{23}$
$\text{C}_{12}\text{H}_{26}$	Dodecane	+214.5	- 12	Dodecyl	$\text{C}_{12}\text{H}_{25}$
$\text{C}_{13}\text{H}_{28}$	Tridecane	+234	- 6.2	Tridecyl	$\text{C}_{13}\text{H}_{27}$
$\text{C}_{14}\text{H}_{30}$	Tetradecane	+252.5	+ 5.5	Tetradecyl	$\text{C}_{14}\text{H}_{29}$
$\text{C}_{15}\text{H}_{32}$	Pentadecane	+270.5	+ 10	Pentadecyl	$\text{C}_{15}\text{H}_{31}$
$\text{C}_{16}\text{H}_{34}$	Hexadecane	+287.5	+ 19	Hexadecyl	$\text{C}_{16}\text{H}_{33}$
$\text{C}_{17}\text{H}_{36}$	Heptadecane	+303	+ 22.5	Heptadecyl	$\text{C}_{17}\text{H}_{35}$
.	.	.	.	.	.
.	.	.	.	.	.
.	.	.	.	.	.
.	.	.	.	.	.
$\text{C}_{60}\text{H}_{122}$	Hexacontane	....	+101	Hexacontyl	$\text{C}_{60}\text{H}_{121}$
.	.	.	.	.	.
.	.	.	.	.	.
.	.	.	.	.	.
.	.	.	.	.	.
$\text{C}_n\text{H}_{2n+2}$	Alkane	....	....	Alkyl	$\text{C}_n\text{H}_{2n+1}$

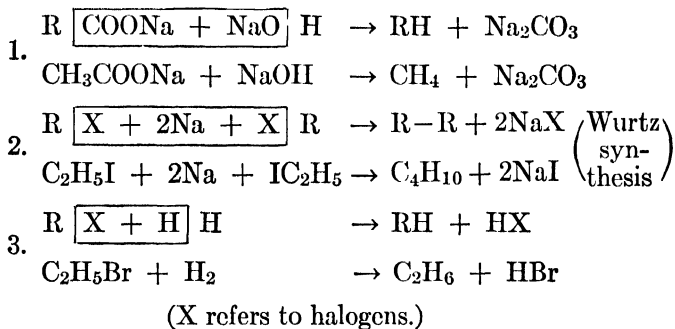
\* A fairly complete table is given at this point to illustrate to what extent a series has been investigated. In the other portions of the book where tables will be given, only the first few members of a series will be included.



spoken of as an "alkyl group." The alkyl group is represented by the letter "R."

Lower members have anesthetic properties while the higher ones beginning with  $C_{12}H_{26}$  have no physiological effects.

### General Methods of Preparation.



**General Properties.**—The paraffins are insoluble in, and lighter than water, and soluble in alcohol, ether, chloroform, benzene, etc. As a rule, their odor is rather pleasant. They are flammable.

**General Chemical Properties.**—All the paraffins are very stable and inactive. At ordinary temperature they are not acted upon by nitric, sulfuric, hydrochloric or chromic acids, or sodium hydroxide. Chlorine reacts in sunlight to form substitution products. Bromine reacts less readily. Iodine does not react at all. (The student will be puzzled at this point to explain how the various iodide compounds used in the *Wurtz* synthesis for paraffins are prepared. We must refer him to the chapters on unsaturated hydrocarbons—p. 34—and alcohols—p. 57—for an answer.)

**Petroleum or Crude Oil.**—The history of the development of the petroleum industry in the United States is instructive. The Indians in Western Pennsylvania first discovered oil floating on surface waters. By them it was used as a remedy for all physical ills. In the middle of the last century, it occurred to a Colonel Drake that, since oil came to the surface of springs, it was probably present in much larger quantities beneath the earth's surface. He thereupon proceeded to drill a well near Oil Creek, Pa. and, before he had dug 100 feet, oil came to the surface in such quantities that all of it could not be collected.

The industrial importance of petroleum is recognized the world over. Coal alone takes precedence over it as a fuel. It is largely, though not entirely, made up of hydrocarbons, but not all the hydrocarbons belong to the paraffin series—the series we have studied in the present chapter. Some of them belong to a type of hydrocarbons with which we shall become acquainted in the next chapter.

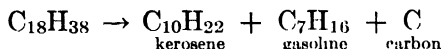
Petroleum is found in many parts of the world, but more particularly in the United States (Pennsylvania, California and Texas), Mexico, Russia (the Baku region), Roumania and Persia. The natural product is usually dark in color, with a characteristic odor, and with a specific gravity that is usually, but not always, less than water. It may be regarded as a mixture of substances, mostly hydrocarbons.

The various products derived from petroleum are obtained by means of fractional distillation, the first fraction consisting of products which pass into the distillate below  $200^{\circ}$ , the second, those that pass over between  $200^{\circ}$ – $275^{\circ}$ , and the third, those which pass over above  $275^{\circ}$ . Each fraction is again redistilled and divided into more fractions, ultimately yielding substances of commercial value. In many refineries the division into fractions is based on specific gravity.

The light oils (up to  $200^{\circ}$ ) include petroleum ether, benzine, gasoline and ligroin; the illuminating oils (from  $200^{\circ}$ – $275^{\circ}$ ) include kerosene; and the lubricating oils ( $275^{\circ}$  and up) include spindle, machine and cylinder oils, etc. In addition, many products of commercial value are obtained, such as vaseline, paraffin, etc.; and the tar residue in the still is used in road-making, artificial asphalt, roofing, etc. If the temperature is high enough, petroleum coke in the place of tar is formed. Due to its high purity, this coke finds extensive use in the manufacture of electrodes.

Commercially, the most important product obtained from petroleum is gasoline, a mixture of hydrocarbons of relatively low molecular weight, such as pentane, hexane, heptane, etc. The process of purification consists of treating the gasoline with sulfuric acid—incidentally one of the most important uses for this acid—whereby many objectionable impurities are removed; the sulfuric acid in turn being removed by washing with water and subsequently with sodium hydroxide solution.

By a careful study of the physico-chemical reactions involved (such as temperature and pressure), American chemists have developed methods of increasing the yield of gasoline. The "cracking" process, used so extensively to-day, consists in breaking up the more complex into the simpler hydrocarbons; for example,



In this way fuel oil (b.p. 275°–350°) is converted into the simpler hydrocarbons. At the present time approximately one-third of the gasoline being produced is derived from cracking heavy oils.

Albolene, nujol and petrolatum are petroleum products used extensively in medicine as intestinal lubricants, and, in pharmacy, as bases for ointments, salves, etc.

Recently, Bergius has perfected a process for the "liquefaction of coal" so that from 50–60 per cent of the latter can be transformed into oil by hydrogenation under high pressure; and Fischer has synthesized hydrocarbons from carbon monoxide and hydrogen at atmospheric pressure and at relatively low temperature.

(Times have changed, indeed. Less than thirty years ago, kerosene cost more than gasoline; the latter, in fact, was regarded little more than a nuisance. To-day it would be hard to conceive of many substances more valuable in commerce than gasoline. Wherever minute quantities of the fuel can be found, it is carefully extracted. Even the small amount found in natural gas is extracted and recovered. Gasoline recovered from the gas that comes from a producing oil well is known as "casinghead" gasoline.)

The chart facing p. 29 outlines the salient features of petroleum refining at a typical plant and names the important commercial products obtained.

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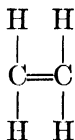
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An eight-reel motion picture "The Story of Petroleum" can be secured, free of charge, from the Bureau of Mines, Pittsburgh, Pa.

## CHAPTER III

### UNSATURATED HYDROCARBONS OR OLEFINS AND ACETYLENES

So far we have been dealing with hydrocarbons that are saturated. When bromine comes in contact with a hydrocarbon of the methane series,  $C_nH_{2n+2}$ , it can enter the compound by substitution only, not by addition; that is, by eliminating one or more hydrogen atoms from the molecule and substituting other atoms, but not by adding an outside atom without any elimination. In this chapter we take up two series of unsaturated compounds, where, as we shall see, atoms can enter the molecule without others leaving it. One series is known as the **olefins**,  $C_nH_{2n}$ , characterized by



and the other, the **acetylenes**,  $C_nH_{2n-2}$ , characterized by



(The student must not draw the conclusion that because there is more than one bond between two atoms, the union between such atoms is correspondingly stronger. On the contrary, since bonds represent strains, the greater the number of bonds between any two carbon atoms, the greater the strain, and hence the greater the chemical reactivity of the compound; so that ethylene is more reactive than ethane and acetylene more than ethylene.)<sup>1</sup>

<sup>1</sup> The instructor may illustrate these "strains" by the use of *Kekulé* models.

OLEFIN SERIES,  $C_nH_{2n}$ —ALKENES

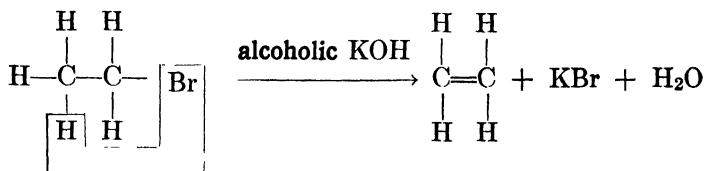
$CH_2$	(hypothetical)	Methylene
$C_2H_4$		Ethylene or ethene
$C_3H_6$		Propylene or propene
$C_4H_8$		Butylene or butene
$C_5H_{10}$		Amylene
etc. (Compare with the paraffins, p. 26.)		

These compounds constitute an homologous series, just as the paraffins, for there is the same difference between any two consecutive members— $CH_2$ ; but it will be noticed that the corresponding olefins have two hydrogen atoms less than the paraffins. The simplest known member of the olefin series, ethylene, combines with chlorine to form an oil ( $C_2H_4Cl_2$ ); hence the name **olefin** ("oil-forming").

In naming these compounds, we change the ending *ane* of the paraffin containing the same number of carbon atoms into *ylene* or *ene*; e.g.,  $C_2H_6$  (ethane)— $C_2H_4$  (ethylene or ~~ethene~~).

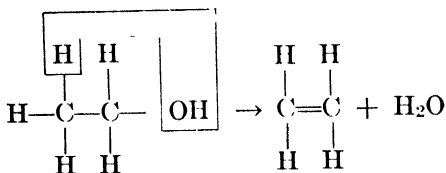
We shall describe one member of this series, ethylene, in some detail, and the general characteristics of the other members can be gleaned from a study of this one.

**Preparation of Ethylene,  $C_2H_4$ .**—One method is by the action of an alcoholic solution of sodium or potassium hydroxide on ethyl bromide, a method of preparation that gives us an insight into the structure of the compound:



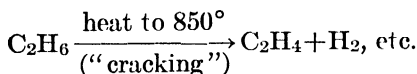
If, instead of using an alcoholic solution of sodium or potassium hydroxide, we use an aqueous solution, ethyl alcohol,  $C_2H_5OH$ , is produced (p. 54).

Another is to treat ethyl alcohol with a strong dehydrating agent, such as  $P_2O_5$  or  $H_2SO_4$ .

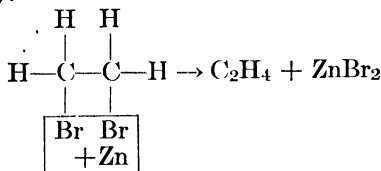


(An alcohol contains an OH group; see p. 49.)

Ethylene is now obtained commercially from ethane, which in turn is derived from natural gas (see chart facing p. 142):



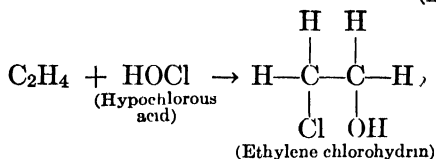
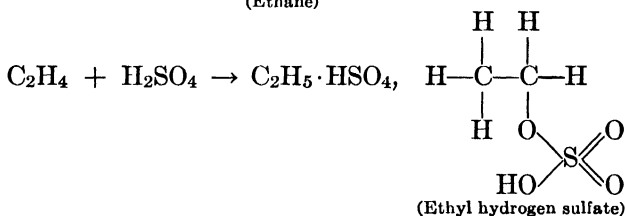
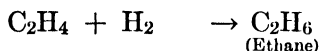
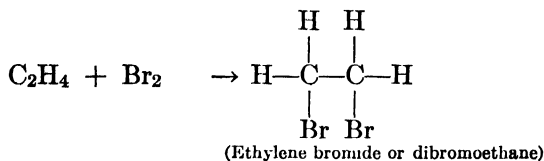
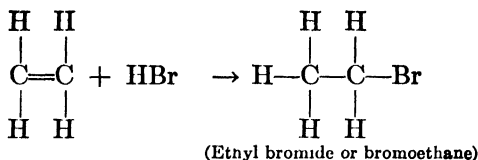
Also, by the action of sodium or zinc on ethylene bromide (dibromoethane):



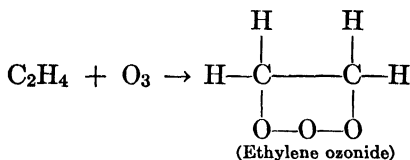
( $\text{C}_2\text{H}_4\text{Br}_2$  may be regarded as ethylene,  $\text{C}_2\text{H}_4$ , to which two bromine atoms have been added; or ethane, in which two of the hydrogens attached to different carbon atoms are replaced by bromine.)

**Properties.**—Ethylene is a colorless gas with a sweetish odor. It burns with a smoky, luminous flame, and forms explosive mixtures with air. It is present in coal gas to the extent of 4–6 per cent, and is partially responsible for its luminosity. It is produced, therefore, in the destructive distillation of coal. Recently, Dr. Luckhardt, of the University of Chicago, has shown that ethylene is a powerful anesthetic and has even some advantages over nitrous oxide. Recently, ethylene has also been introduced in California for coloring mature citrus fruits (oranges, lemons, etc.). For industrial developments of ethylene chemistry see chart facing p. 142.

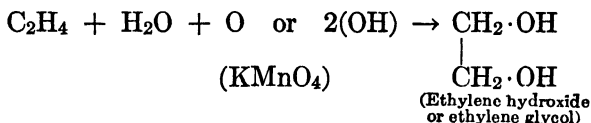
The characteristic properties of ethylene are dependent upon the presence of a double bond, and therefore upon its unsaturated character. It combines with halogen acids, with halogens, with hydrogen, with sulfuric acid, with hypochlorous acid, with ozone, etc., and is used as the starting material for the preparation of many organic compounds.



(Whenever a compound has a halogen atom attached to a carbon atom, and an OH group to another carbon atom, we speak of it as a "halohydrin"; hence chlorohydrin, as in the above.)

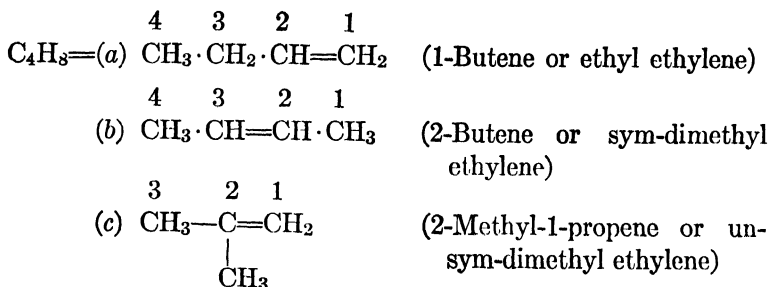
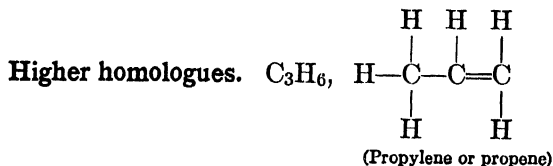


A test sometimes used for the detection of the double bond is based on the action of very dilute potassium permanganate; the violet color of the permanganate disappears, due to its decomposition. The reaction may be represented thus:





(The student must clearly understand that  $C_2H_4$  alone represents the gas ethylene, but  $C_2H_4$  may be present as a divalent group in a compound; for example, ethylene bromide,  $C_2H_4Br_2$ .)



(In naming an olefin, a number is employed to indicate the position of the double bond; this number denotes the unsaturated carbon atom which lies nearest to the end of the chain.)

Sometimes the Greek letter  $\Delta$  is used to denote the double bond, so that (a), (b) and (c) may also be written  $\Delta^1$ -Butene;  $\Delta^2$ -Butene; 2-Methyl- $\Delta^1$ -propene. (The methods of preparation and properties are analogous to those given for ethylene.)

#### ACETYLENE SERIES— $C_nH_{2n-2}$ —ALKINES

- $C_2H_2$  Acetylene or ethine  
 $C_3H_4$  Propyne or methyl acetylene  
 $C_4H_6$  Butyne or dimethyl acetylene or ethyl acetylene  
 etc.

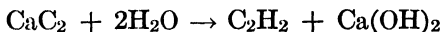
These also constitute a homologous series. The members contain two hydrogen atoms less than the corresponding members of the olefins, or four hydrogen atoms less than the corresponding paraffins. They are named by changing the *ane* ending of the paraffins into *ine*, so that ethane,  $C_2H_6$ , for example, becomes

ethine,  $C_2H_2$ . This series is known as the **acetylene** series, for acetylene is the most important member.

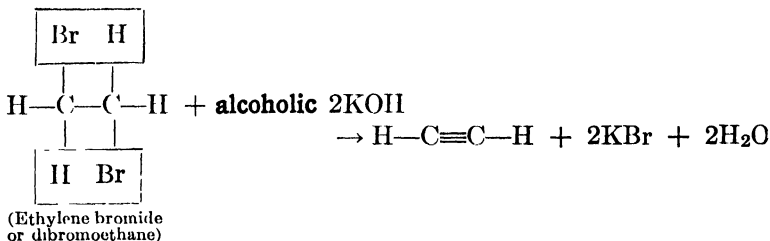
As before, we shall discuss a typical member in some detail.

**Acetylene**,  $C_2H_2$ , has the formula  $H-C\equiv C-H$ , which shows it to have a triple bond and therefore indicates that it is even more unsaturated than ethylene,<sup>1</sup> a view which is confirmed by a study of its reactions. Acetylene is an extremely reactive compound. Its formula may also be written as  $=C=CH_2$  (p. 40).

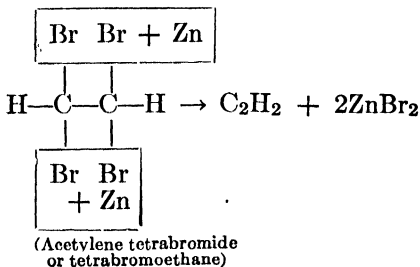
**Preparation.**—One method is probably already familiar to the student. It is the action of water on calcium carbide:



Another is similar to a method used under the olefins:



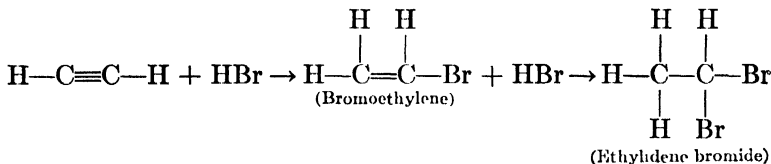
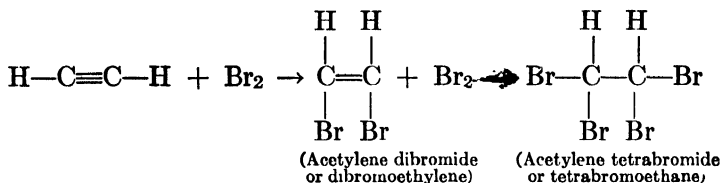
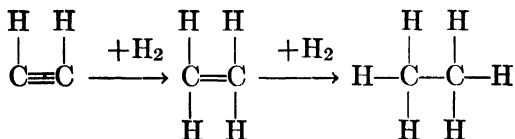
So is the following:



Acetylene is a colorless gas. When mixed with air in a special type of burner, it burns with a very brilliant white light and is used for illuminating purposes. When burned it gives out a large amount of heat. This is made use of in the oxy-acetylene torch (for cutting steel, etc.) wherein acetylene, supplied under pressure, is burned in the presence of oxygen. The gas is apt to explode if stored under pressure, but can be safely handled if it is first dissolved in acetone (as in "prestolite" tanks). Liquid acetylene is highly unstable and highly explosive.

<sup>1</sup> The instructor may illustrate this by the use of the *Kekulé* models.

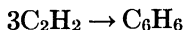
**Properties.**—Since acetylene is an unsaturated compound, it will form addition products (like ethylene), but since it is more unsaturated than ethylene, it can add to itself more atoms than  $C_2H_4$ .



( $\text{CH}_2\text{Br} \cdot \text{CH}_2\text{Br}$ , ethylene bromide, or symmetrical dibromoethane, is isomeric with  $\text{CH}_3 \cdot \text{CHBr}_2$ , ethylidene bromide, or unsymmetrical dibromoethane.)

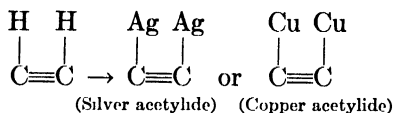
(The student must clearly understand that  $\text{C}_2\text{H}_2$  alone represents the gas acetylene, but  $\text{C}_2\text{H}_2$  may be present as a divalent group in a compound; for example, acetylene dibromide,  $\text{C}_2\text{H}_2\text{Br}_2$ . It may also be present as a tetravalent group; for example, acetylene tetrabromide,  $\text{C}_2\text{H}_2\text{Br}_4$ .)

When acetylene is passed over finely divided nickel, three molecules of it polymerize to form benzene:

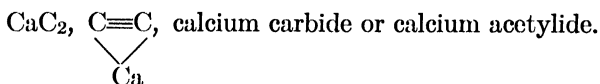


(**Polymers** are substances having the same percentage composition, but different molecular weights.  $\text{C}_2\text{H}_2$  and  $\text{C}_6\text{H}_6$  have the same percentage of carbon and of hydrogen, but the molecular weight of acetylene is 26 and that of benzene is 78.)

Acetylene combines with ammoniacal silver chloride or copper chloride solution to form metallic derivatives (acetylides):



Many of them are highly unstable and explosive, particularly in the dry state. In fact, many of the explosions involving acetylene are due to the formation of these acetylides.



### *Higher homologues.*

$\text{C}_3\text{H}_4$ ,  $\text{CH}_3 \cdot \text{C} \equiv \text{CH}$  (Propyne or methyl acetylene)

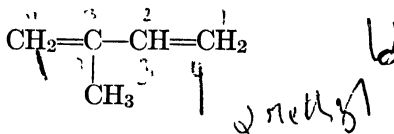
$\text{C}_4\text{H}_6$ , (a)  $\text{CH}_3 \cdot \text{C} \equiv \text{C} \cdot \text{CH}_3$  (2-Butyne or dimethyl acetylene)

(b)  $\text{C}_2\text{H}_5\text{C} \equiv \text{CH}$  (1-Butyne or ethyl acetylene)

(The general properties correspond to those of acetylene, except that only the compounds with the structure  $-\text{C} \equiv \text{C}-\text{H}$  can form acetylides.)

(At this point review the nomenclature of hydrocarbons on the "Organic Type Formula" chart, p. 16.)

Compounds containing two double bonds are isomeric with those containing one triple bond; for example,  $\text{CH}_3-\text{C} \equiv \text{CH}$  is isomeric with  $\text{CH}_2=\text{C}=\text{CH}_2$ . The name of a compound having one double bond ends in *ene*; a compound having two double bonds has the ending *diene*, e.g.,  $\text{CH}_2=\text{C}=\text{CH}_2$  is propadiene. The most important among the compounds containing two double bonds is **isoprene**

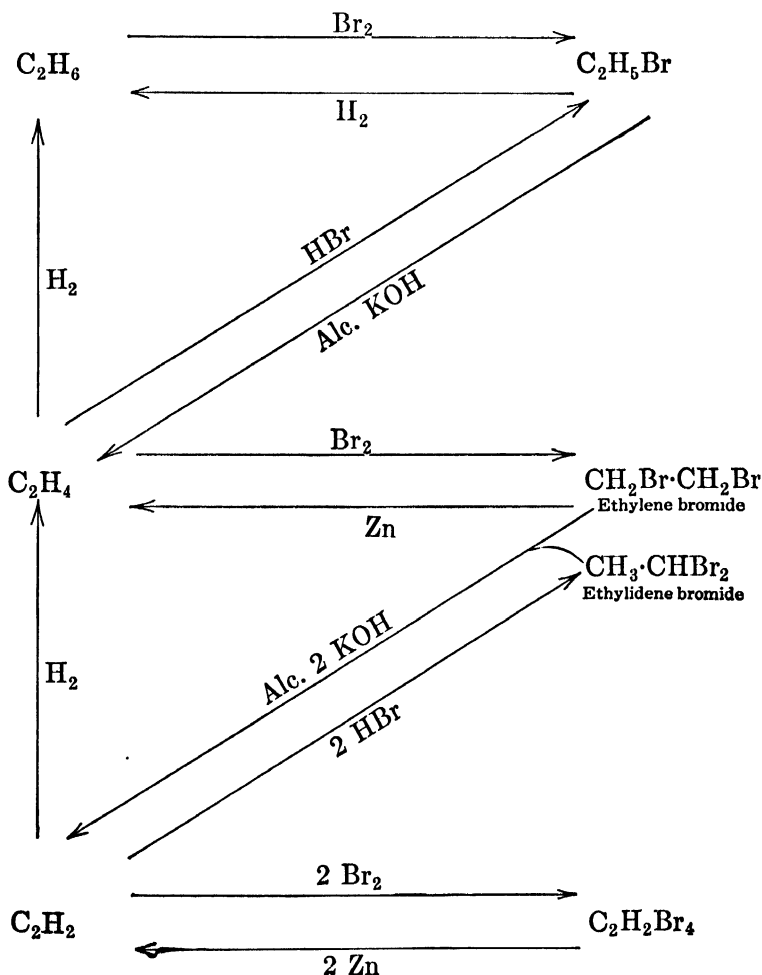


or 2-methyl-1,3-butadiene, which has been shown to be one of the decomposition products of caoutchouc (natural rubber), and which is obtained by the distillation of the latter. Isoprene itself (in presence of catalysts, as HCl, Na, etc.) has been polymerized back into a substance resembling caoutchouc, the resulting product showing some striking resemblances to natural rubber. The synthesis of rubber on an industrial scale, however, is a problem that still awaits solution. There seems to be little doubt in the minds of chemists that isoprene, or some substance closely analo-

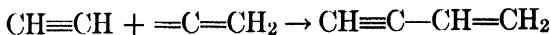
gous to it in structure, will prove to be the starting-point of such a synthesis.

It has recently been shown that rubber when stretched shows an X-ray spectrogram similar to those of ordinary well-defined crystals. All X-ray interferences agree to a rectangular-rhombic crystal with a basic cell of  $(C_5H_8)_8$ . The number of combined molecules needed to produce the interferences are about 2000.

Very recently a very promising method of synthesizing rubber-like substances in the laboratory has been announced. In the

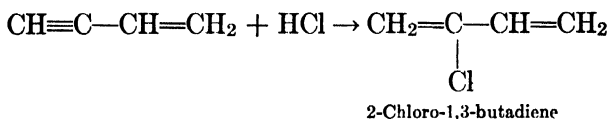


presence of complex cuprous salts, acetylene may be polymerized to vinylacetylene:



(The  $\text{CH}_2=\text{CH}$  monovalent group is known as the vinyl group.)

When vinylacetylene is treated with hydrogen chloride, **chloroprene** is obtained:



By allowing the chloroprene to stand at room temperature and in the absence of direct light, it gradually polymerizes to a stiff, pale yellow, elastic mass, and resembles a "completely vulcanized soft rubber."

The diagram on page 39 makes clear some of the interconnections of compounds already discussed.

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## CHAPTER IV

### HALOGEN DERIVATIVES OF HYDROCARBONS

WE have already observed that the action of chlorine on methane gives us the following substitution products:  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$  (p. 19). It ought to be possible to prepare any one of these substances by employing the proper amount of chlorine. (Bromine is less reactive than chlorine. It produces analogous substitution products. Iodine does not react with methane.) It is found in practice, however, that a series of simultaneous reactions occur, yielding a mixture of chlorides. (Mention may be made at this point of the many attempts to produce chloroform,  $\text{CHCl}_3$ , on a commercial scale by the action of chlorine on methane; and also of methyl chloride,  $\text{CH}_3\text{Cl}$ , by a similar reaction. Methyl chloride can be easily hydrolyzed to methanol or wood alcohol,  $\text{CH}_3\text{OH}$ , and thus the synthetic methanol could then be prepared starting from natural gas, which contains methane. Research is being carried on at the present time along these lines.)

**Monohalogen Derivatives of the Paraffins.**—An alkyl halide (or monohalogen derivative of a hydrocarbon, p. 43), may be regarded as a saturated hydrocarbon in which one of the hydrogens is replaced by a halogen (F, Cl, Br, I). The following will make this clear:

$\text{C}_n\text{H}_{2n+2}$	$\text{C}_n\text{H}_{2n+1}$ Group	$\text{C}_n\text{H}_{2n+1}\text{X}$ (alkyl halide)
Methane, $\text{CH}_4$	Methyl Group, $\text{CH}_3$	Methyl chloride, $\text{CH}_3\text{Cl}$
Ethane, $\text{C}_2\text{H}_6$	Ethyl Group, $\text{C}_2\text{H}_5$	Ethyl bromide, $\text{C}_2\text{H}_5\text{Br}$
etc.	etc.	etc.
<b>Alkane, <math>\text{RH}</math></b>	<b>Alkyl Group, <math>\text{R}</math></b>	<b>Alkyl halide, <math>\text{RX}</math></b>

( $\text{RX}$  is the type formula for an alkyl halide.)

## ALKYL HALIDES

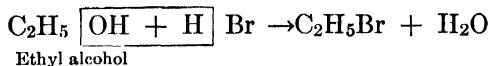
Chloride	For- mula	B. P. ° C.	Bromide	For- mula	B. P. ° C.	Iodide	For- mula	B.P. ° C.
Methyl	CH <sub>3</sub> Cl	-24	Methyl	CH <sub>3</sub> Br	4.5	Methyl	CH <sub>3</sub> I	43
Ethyl	C <sub>2</sub> H <sub>5</sub> Cl	12.5	Ethyl	C <sub>2</sub> H <sub>5</sub> Br	38.4	Ethyl	C <sub>2</sub> H <sub>5</sub> I	72
Propyl	C <sub>3</sub> H <sub>7</sub> Cl	46.5	Propyl	C <sub>3</sub> H <sub>7</sub> Br	71	Propyl	C <sub>3</sub> H <sub>7</sub> I	102
Isopropyl	C <sub>3</sub> H <sub>7</sub> Cl	36.5	Isopropyl	C <sub>3</sub> H <sub>7</sub> Br	59	Isopropyl	C <sub>3</sub> H <sub>7</sub> I	89
n-Butyl *	C <sub>4</sub> H <sub>9</sub> Cl	77.5	n-Butyl	C <sub>4</sub> H <sub>9</sub> Br	101	n-Butyl	C <sub>4</sub> H <sub>9</sub> I	129
etc.			etc.			etc.		

\* n- is the abbreviation for "normal"

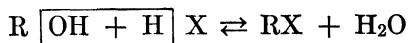
In each group the specific gravities decrease as the molecular weights increase. The specific gravity increases as we pass from a certain alkyl chloride to the bromide and in turn to the iodide having the same alkyl group.

These halides are insoluble in water but soluble in ether, benzene and alcohol. The halides are generally colorless liquids with a pleasant odor. On standing, they develop color (this is especially true of the iodides), due to decomposition, and are generally kept in amber-colored bottles.

**General Methods of Preparation.**—By the action of a halogen acid on an alcohol in presence of a dehydrating agent. (An alcohol contains the —OH group. Examples of alcohols are C<sub>2</sub>H<sub>5</sub>OH, ethyl alcohol, C<sub>3</sub>H<sub>7</sub>OH, propyl alcohol, and in general ROH.)



Or, more generally,

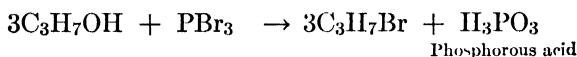
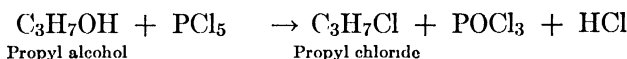


(Whenever throughout the text "R" is used in an equation, it implies that the reaction is a general one; or, in other words, is a "type" reaction. This does not necessarily imply that where specific examples are given, they cannot illustrate general type reactions. As a matter of fact, in most cases the specific examples do illustrate type reactions.)

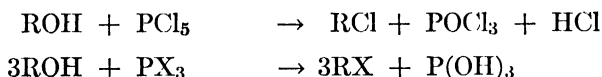


This reaction is analogous to the "neutralization" reaction in inorganic chemistry, such as  $\text{Na} \boxed{\text{OH} + \text{H}} \text{Cl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ . However, the production of  $\text{NaCl}$  is an instantaneous reaction, whereas the formation of  $\text{RX}$  is a comparatively slow process; and in the production of  $\text{RX}$  we must have a dehydrating agent present to remove the water as fast as it is formed, otherwise the reaction is reversible.

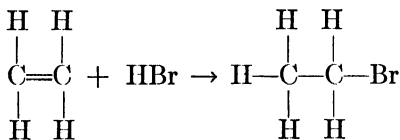
Another method is the action of a phosphorus halogen compound on an alcohol; e.g.,



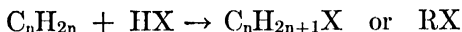
or



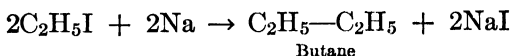
A third method consists in the addition of halogen acids to unsaturated compounds; e.g.,



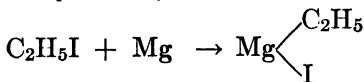
or



**Properties.**—The halogen compounds react with many reagents to form diverse products. The following are examples of a number of type reactions:

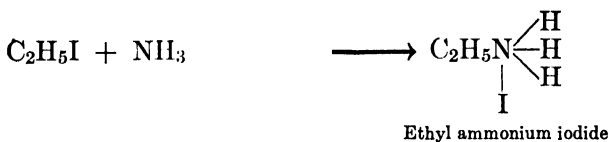
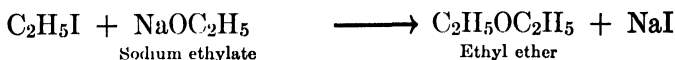
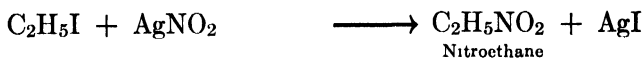
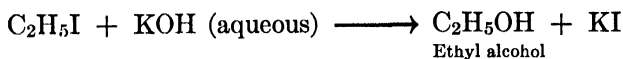
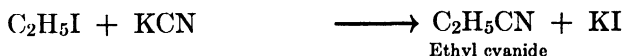


(The *Wurtz* Synthesis.)



Magnesium ethyl iodide (I)

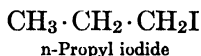
Compounds of type (I) are known as *Grignard's reagent*, the general type formula being  $R \cdot Mg \cdot X$ .



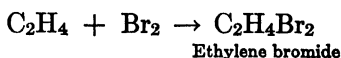
(At this stage the student is not expected to memorize these equations, but rather, by examining them, to understand why the halides find such extensive applications.)

(Many of the reactions illustrated are of the "double decomposition" type.)

**Methyl chloride**,  $CH_3Cl$ , and **Ethyl chloride**,  $C_2H_5Cl$ , are used as local anesthetics, for when sprayed upon the skin the liquids evaporate rapidly, thereby cooling the tissue. To some extent they are used for refrigerating purposes. Ethyl chloride is used in the preparation of lead tetraethyl (p. 199). **Ethyl bromide**,  $C_2H_5Br$ , has also been used as an anesthetic.



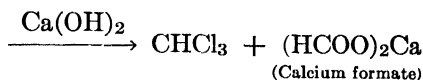
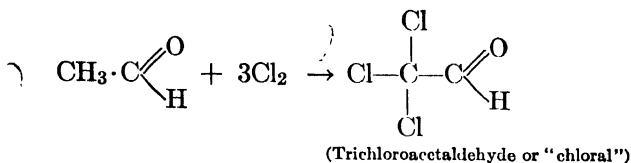
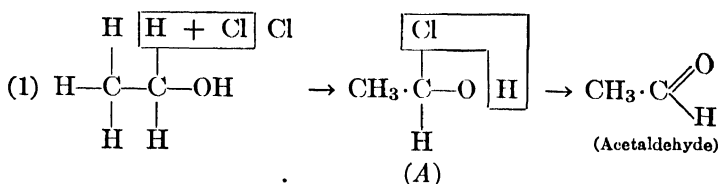
*Dihalogen Derivatives of the Paraffins.*—These have the general formula  $C_nH_{2n}X_2$  ( $C_2H_4Br_2$ , dibromoethane, and  $C_3H_6Cl_2$ , dichloropropane, are examples). They are usually prepared by the addition of a halogen to an unsaturated hydrocarbon:



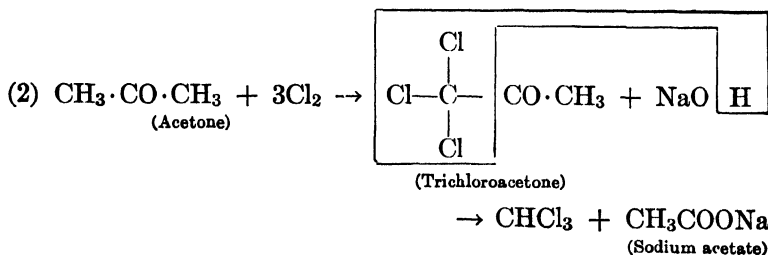
( $\text{CH}_2\text{I}_2$  is of interest since it is the heaviest organic liquid, its specific gravity being 3.292 at  $18^\circ$ , ethylene dichloride,  $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ , is used as a fumigant and also as a solvent for oils, fats, etc., and for the preparation of ethylene glycol (p. 63).

*Trihalogen Derivatives of the Paraffins.*—The important compounds of this type are chloroform,  $\text{CHCl}_3$ , bromoform,  $\text{CHBr}_3$ , and iodoform,  $\text{CHI}_3$ .

**Chloroform**,  $\text{CHCl}_3$ , is prepared by the action of chlorine (in the form of bleaching powder) on (1) ethyl alcohol or (2) acetone.



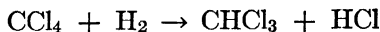
(A) represents a hypothetical compound, or at least one which has not so far been isolated. Its instability, it would seem, is due to the Cl and OH groups being attached to the same carbon atom. The type formula for an aldehyde is  $\text{R}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{H} \end{array}$ . We shall discuss these aldehydes later, p. 73.



Acetone is the simplest of the group of compounds known as "ketones." Their type formula is  $R \cdot CO \cdot R$  (p. 73).

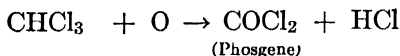
In practice the necessary chlorine is obtained by the use of bleaching powder.

Chloroform is now made on a large scale by the reduction of  $CCl_4$ :



Chloroform (trichloromethane) is a colorless liquid with a sweet taste and suffocating odor. Its b.p. is  $61^\circ$ . It is slightly soluble in water. It is non-flammable. Its anesthetic properties were discovered by Dr. Simpson of Edinburgh, in 1848.

Chloroform has a tendency to decompose when exposed to air and light:

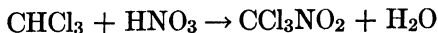


To prevent this, ethyl alcohol (to the extent of about 1 per cent) is added to it. It is usually kept in dark (amber) colored bottles.

Pure  $CHCl_3$  does not react with silver nitrate, but, if any decomposition has occurred, a precipitate of  $AgCl$  forms.

( $CHCl_3$  alone is now rarely used as an anesthetic, for ether and ethylene have largely taken its place. Sometimes a mixture of ether and chloroform is used. The advantage of ether over chloroform is that it is less dangerous and the after-effects are not so pronounced.)

Acetone and chloroform combine to form **chloretone**,  $(CH_3)_2C(OH) \cdot CCl_3$ , used extensively as a hypnotic, anodyne and preservative. Chloroform reacts with concentrated nitric acid to form **chloropicrin**, or **nitrochloroform**, a substance that was used in the late war as a lachrymator ("tear gas"):



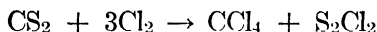
When prepared on a large scale, the chloropicrin is made by the action of bleaching powder on picric acid (p. 279).

Chloroform is sometimes used as a "preservative" for the prevention of bacterial growth, though for most purposes toluene has largely taken its place. Chloroform is an excellent solvent for many organic compounds. It dissolves fats, rubber, etc.

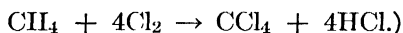
**Bromoform**,  $\text{CHBr}_3$ , is prepared in a manner quite analogous to chloroform. Its anesthetic properties are less marked.

**Iodoform** (triiodomethane),  $\text{CHI}_3$ , is prepared by adding iodine to a warm solution of sodium carbonate containing alcohol or acetone—in principle analogous to the preparation of chloroform. The odor of iodoform is not only characteristic, but powerful, hence the reaction is used as a test for either alcohol or acetone. Iodoform is a powerful antiseptic and disinfectant. (The antiseptic properties are due to its gradual decomposition with the liberation of iodine.)

**Tetrahalogen Derivatives of the Paraffins**,  $\text{CF}_4$ ,  $\text{CCl}_4$ ,  $\text{CBr}_4$  and  $\text{CI}_4$ . Of these, only the second, **carbon tetrachloride**, is important. It is made commercially by passing chlorine into carbon disulfide, using iron, iodine or antimony pentasulfide as a catalyst:



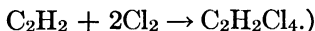
(We have already mentioned the production of  $\text{CCl}_4$  from methane by the action of chlorine:



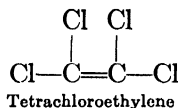
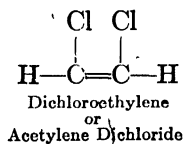
Carbon tetrachloride is a colorless liquid with an ethereal odor. It is a good solvent for gums and resins and is also a constituent of many cleaning solutions. It is an anesthetic, but is not used because of its bad effect on the heart. It is used in fire extinguishers ("Pyrene"). Its vapor produces severe headaches.

**Dichlorodifluoromethane**,  $\text{CCl}_2\text{F}_2$ , is now used as a refrigerant.

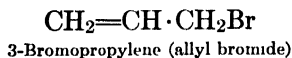
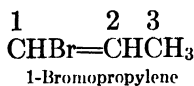
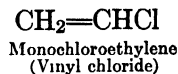
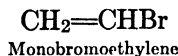
(During the past few years a number of chlorinated paraffins, used as solvents, have been prepared on a commercial scale. One such is tetrachloroethane, made by the action of chlorine on acetylene:



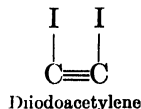
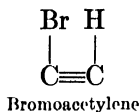
**Halogen Derivatives of Unsaturated Hydrocarbons.**—The names and structures of a few of these will be given:



(These are used as solvents.)



( $\text{CH}_2=\text{CH} \cdot \text{CH}_2$  is known as the allyl group.)



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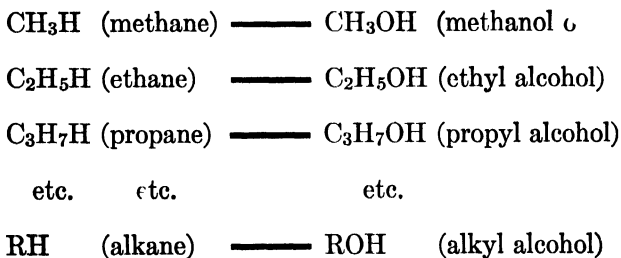
## CHAl

## ALCO

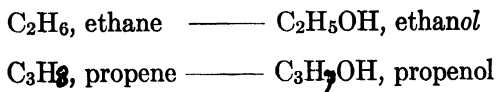
METHANOL, which is methyl (c grain) alcohol, are the two most in to this group.

The alcohols may be considered as or more of the hydrogens are replaced b, also be regarded as derived from water i. gens is replaced by R;  $\text{H—OH} \rightarrow \text{R—O}$

The relationship of the hydrocarbons to here:



**Nomenclature of Alcohols.**—There are a number of system. employed. (1) The ending *e* of the hydrocarbon containing the same number of carbon atoms is changed to the ending *ol*:



(2) The alcohol is named according to the alkyl group it contains:  $\text{C}_2\text{H}_5\text{H}$ , ethane ———  $\text{C}_2\text{H}_5$ , ethyl group ———  $\text{C}_2\text{H}_5\text{OH}$ , ethyl alcohol, or ethyl hydroxide.

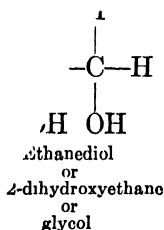
as "carbinol" derivatives:

ol "

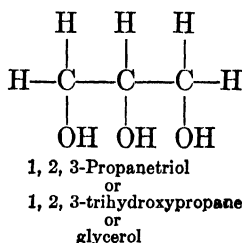
methyl carbinol

, ethyl methyl carbinol

ol in which one of the hydrogen atoms  
ethyl methyl carbinol is carbinol in which  
replaced by  $C_2H_5$  and another by  $CH_3$ .)  
contain more than one OH group provided they  
are on different carbon atoms; *e.g.*

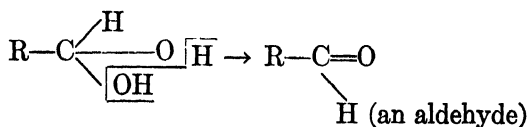


etc.



We shall see in a later chapter that the sugars contain several OH groups.

(Two or more OH groups attached to the same carbon atom give rise, as a rule, to unstable compounds:

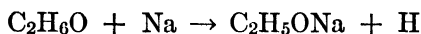


the unstable dihydroxy compound being converted into an aldehyde. We shall explain the oxidation of an alcohol to an aldehyde in this manner.)

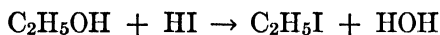


An alcohol with one OH group is monatomic, with two OH groups, diatomic, with three, triatomic, etc.

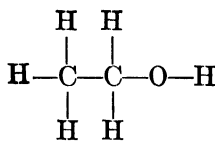
If we take an alcohol, such as ethyl alcohol,  $C_2H_6O$ , and treat it with sodium, only one atom of hydrogen (out of the six present) is liberated:



This particular atom of hydrogen obviously differs in some way from the other five atoms. The possibility that this difference is due to a difference in position within the molecule is borne out by the fact that when we treat the alcohol with, say, hydrogen iodide, one atom of iodine replaces one atom of hydrogen and one atom of oxygen,—one iodine, in other words, replaces one hydroxyl group:



It would seem, therefore, as if one hydrogen in ethyl alcohol is attached, not to the carbon atoms (like the other five hydrogen atoms), but to the oxygen atom:



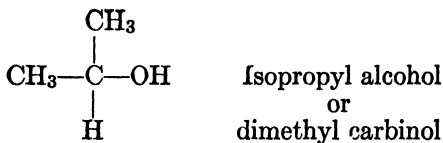
and all the reactions of the many alcohols known (some of which will be discussed presently) strengthen this view.

### Types of Alcohols.

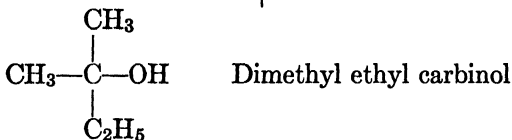
1. The presence of the group  $\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{OH} \\ | \\ \text{H} \end{array}$  indicates a **primary**

**alcohol:** e.g.,  $\text{CH}_3-\text{C} \begin{array}{l} \nearrow \text{H} \\ \rightarrow \text{OH} \\ \searrow \text{H} \end{array}$ .

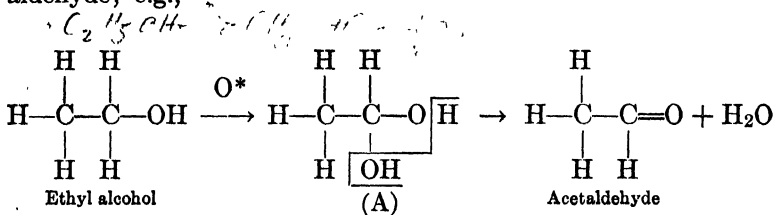
2. The group  $\begin{array}{c} | \\ \text{—C—OH} \\ | \\ \text{H} \end{array}$  indicates a **secondary alcohol**: e.g.,



3. The group  $\begin{array}{c} | \\ \text{—C—OH} \\ | \end{array}$  indicates a **tertiary alcohol**: e.g.,

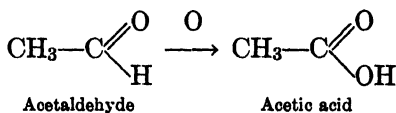


These three types of alcohols yield various oxidation products. When a primary alcohol is oxidized, we first get an aldehyde; e.g.,



(It is believed that (A) is an intermediate compound, though it has not, as yet, been isolated. It has already been pointed out that a compound containing two OH groups attached to the same carbon atom is usually unstable, water splitting off in the manner shown.)

The aldehyde on further oxidation yields the corresponding acid:

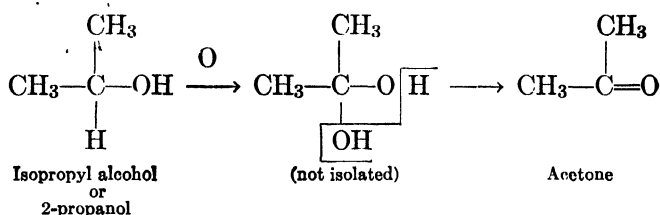


\*O refers to oxidation

(Let us inform the student at this point that the group  $\text{—C}\begin{smallmatrix} \text{O} \\ \text{//} \\ \text{H} \end{smallmatrix}$  is characteristic of aldehydes, and the group  $\text{—C}\begin{smallmatrix} \text{O} \\ \text{//} \\ \text{OH} \end{smallmatrix}$  is commonly characteristic of organic acids.)

We see then that the oxidation of a primary alcohol yields first an aldehyde and then an acid containing the same number of carbon atoms as the original alcohol.

When a secondary alcohol is oxidized we get a ketone; e.g.,

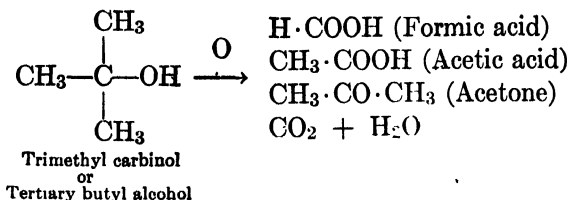


$\begin{array}{l} \text{R} \\ \diagup \\ \text{C=O} \\ \diagdown \\ \text{R} \end{array}$  represents ketones, and acetone is the simplest member of the series. On further oxidation we get acids containing less carbon atoms than the original ketone or alcohol.

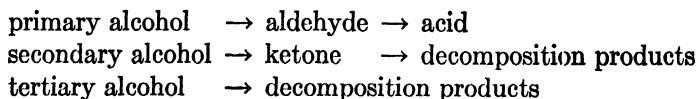
(There are two isomeric propyl alcohols, the normal,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$ , and the iso,  $\text{CH}_3\text{—}\begin{array}{c} \text{H} \\ | \\ \text{C—OH} \\ | \\ \text{CH}_3 \end{array}$ . The latter,

being a secondary alcohol, yields a ketone—acetone—on oxidation; the normal, being a primary alcohol, yields first an aldehyde—propionaldehyde—and then an acid—propionic acid.)

When a tertiary alcohol is oxidized, a mixture of acids and ketones are obtained, each substance formed having less carbon atoms in its molecule than the original tertiary compound: e.g.,

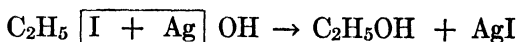


We therefore see that on oxidation

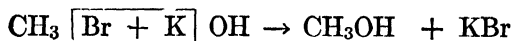


**Methods of Preparation.**—Alcohols are produced in the course of destructive distillation (p. 58) and fermentation (p. 59). Other methods are the following:

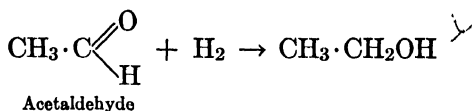
The action of moist silver oxide or aqueous NaOH or KOH solution on an alkyl halogen compound, as



or

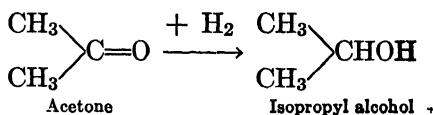


The reduction of aldehydes (yielding primary alcohols); as

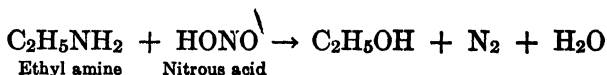


(The student will recall that the oxidation of a primary alcohol yields an aldehyde; we may therefore expect that the reduction of the aldehyde will yield the alcohol. The reducing agent may be sodium amalgam and water, or hydrogen in the presence of nickel, etc.)

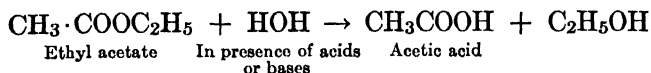
The reduction of ketones (yielding secondary alcohols); as



The action of nitrous acid on a primary amine (that is, a substance formed when one of the hydrogens in  $\text{NH}_3$  is replaced by R, giving  $\text{R} \cdot \text{NH}_2$ ; (see p. 138); as



The hydrolysis of esters; as



(An ester is an acid in which the ionizable hydrogen is replaced by an alkyl group:  $\text{R} \cdot \text{COOH} \rightarrow \text{R} \cdot \text{COOR}$ .)  
 (Acid) (Ester)

Various secondary and tertiary alcohols can be prepared by means of the *Grignard* reaction; e.g.,

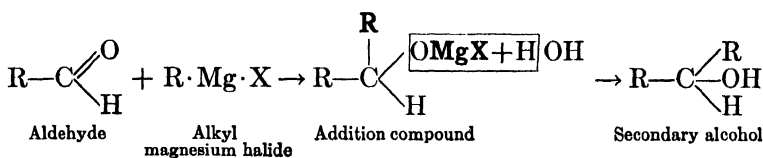


Illustration:

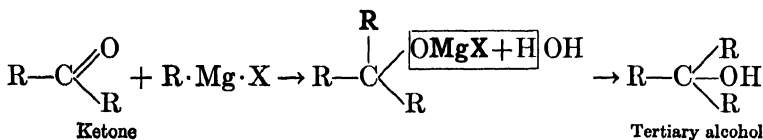
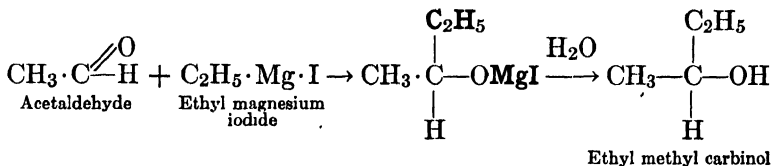
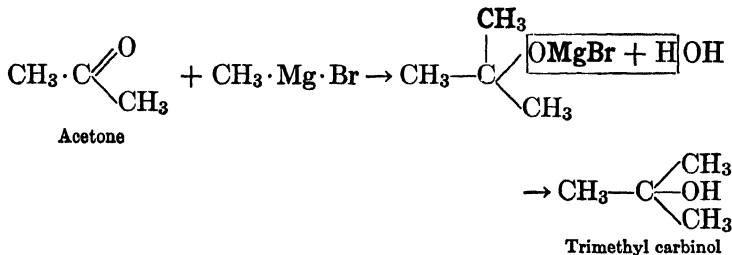
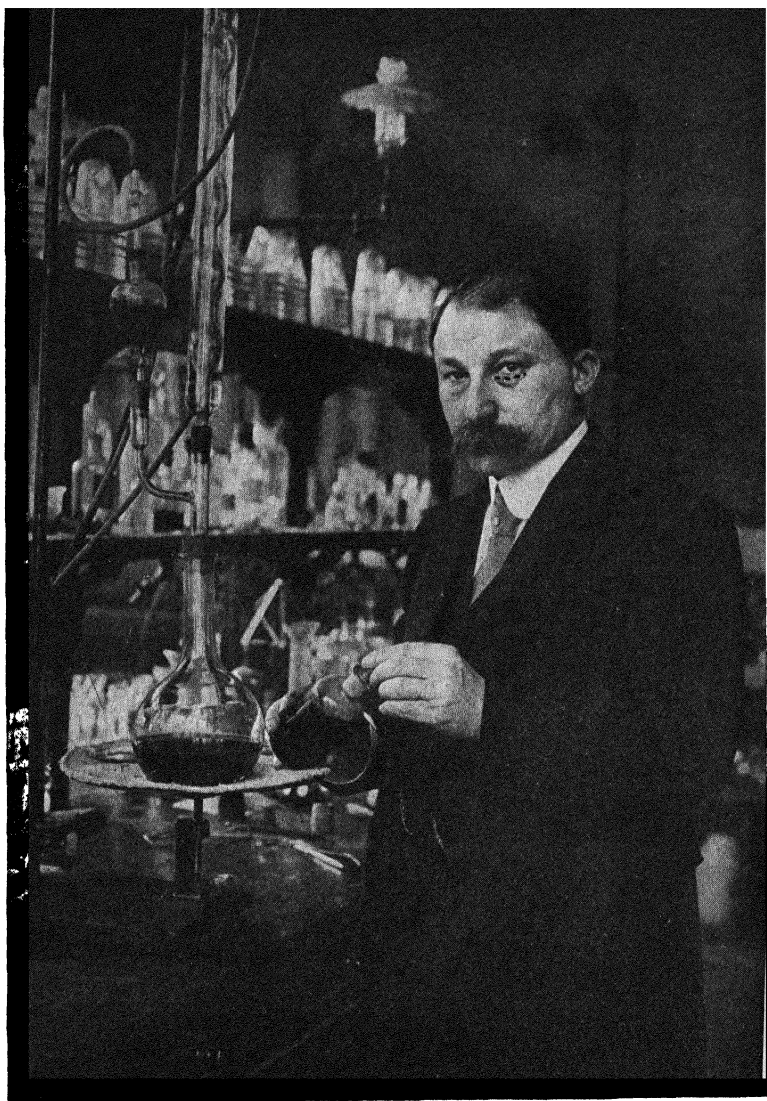


Illustration:



From aldehydes, therefore, we can get secondary alcohols, and from ketones, tertiary alcohols.



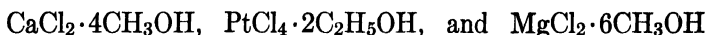
A stylized, handwritten signature of Victor Grignard, written in dark ink. The signature is fluid and cursive, with a long horizontal line extending from the end of the name.

VICTOR GRIGNARD (1871-

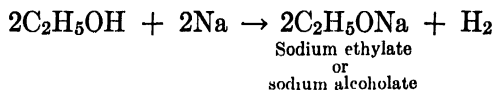
PROFESSOR OF CHEMISTRY AT THE UNIVERSITY OF LYON (FRANCE). HIS DISCOVERY OF THE ORGANO-MAGNESIUM COMPOUNDS AND THEIR REACTIONS, FOR WHICH HE RECEIVED THE NOBEL PRIZE, HAS BEEN OF INESTIMABLE VALUE IN THE SYNTHESIS OF MANY ORGANIC COMPOUNDS.

**Physical Properties.**—The monatomic alcohols are colorless substances. The compounds from  $\text{CH}_3\text{OH}$  to  $\text{C}_4\text{H}_9\text{OH}$  are limpid liquids, those from  $\text{C}_5$  to  $\text{C}_{11}$  are of oily consistency, and from  $\text{C}_{12}$  up are solids. The solubility in water decreases with increase in molecular weight. An increase in the number of OH groups in a compound tends to increase the sweetness; e.g., methanol  $\text{CH}_3\text{OH}$ , is not sweet; glycol,  $\text{C}_2\text{H}_4(\text{OH})_2$  is somewhat sweet; glycerol,  $\text{C}_3\text{H}_5(\text{OH})_3$ , is sweet; and mannitol,  $\text{C}_6\text{H}_8(\text{OH})_6$ , is still sweeter. The lower alcohols have characteristic odors; the  $\text{C}_8$ – $\text{C}_{12}$  have rose- or lily-like odors and are used in perfumery, while the higher ones are practically odorless.

**Chemical Properties.**—The alcohols, like water (which they resemble in many ways), are neither acid nor alkaline in reaction. Like water again, the alcohols combine with compounds to form crystalline products; for example,

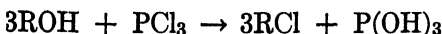
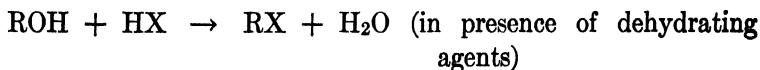


These compounds are said to contain “alcohol of crystallization.” Sodium reacts with alcohol as it does with water, only less violently; e.g.,



As we have seen, the primary alcohols, on oxidation, yield aldehydes and acids; the secondary alcohols, ketones; and the tertiary alcohols, various decomposition products.

The OH group in the alcohol can be replaced by a halogen in a number of ways:



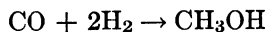
Alcohols combine with acids to form esters: e.g.,

## MONATOMIC ALCOHOLS

Alcohol	Formula
Methyl.....	$\text{CH}_3\text{OH}$
Ethyl.....	$\text{CH}_3 \cdot \text{CH}_2\text{OH}$
<i>n</i> -Propyl.....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2\text{OH}$
Isopropyl.....	$\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_3$
<i>n</i> -Primary butyl.....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2\text{OH}$
<i>n</i> -Secondary butyl.....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_3$
Primary isobutyl.....	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH} \cdot \text{CH}_2\text{OH} \\ \diagup \\ \text{CH}_3 \end{array}$
Trimethyl carbinol (tertiary butyl).....	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}(\text{OH}) \\ \diagup \\ \text{CH}_3 \end{array}$
:	:
:	:
:	:
:	:
Cetyl.....	$\text{C}_{16}\text{H}_{33}\text{OH}$
Myricyl.....	$\text{C}_{30}\text{H}_{61}\text{OH}$

**Methanol,**<sup>1</sup>  $\text{CH}_3\text{OH}$  (also called methyl alcohol, wood alcohol, methyl hydroxide, carbinol, Columbian spirit and wood spirit). This alcohol does not occur free in nature. On a commercial scale it is obtained by the destructive distillation of hard wood (maple, beech, birch, oak, etc.). When wood is heated in retorts to about  $400^\circ$ , we obtain gases (used as fuel under the retorts), an aqueous distillate (known as "pyroligneous acid"), wood tar and charcoal (which remains in the retorts). The wood tar is a source for antiseptics (wood creosote), disinfectants, fuel, road-making, etc. The pyroligneous acid contains the acetic acid, as well as the methanol and acetone. The acetone of commerce is not obtained from this source (see p. 76).

Using a catalytic process, synthetic methanol is now manufactured from carbon monoxide and hydrogen,



The catalyst is zinc oxide; the temperature is about  $400^\circ$  and the pressure about 150 atmospheres.

A very recent process is from the by-products of the ethyl alcohol, butanol, acetone fermentation process (pp. 63, 84). In this fermentation pure hydrogen and carbon dioxide gases are

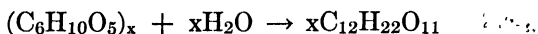
<sup>1</sup> The name "methanol" has now been officially adopted, largely with a view to preventing its use in the place of grain alcohol.



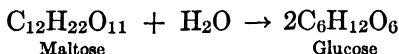
generated and the synthetic methanol process employed involves two steps. An adjustment is made in the relation of hydrogen to carbon dioxide by a simple scrubbing process under pressure, after which the mixture is further compressed and passed over the methanol catalyst at elevated temperature.

**Properties and Uses.**—Methanol is a colorless liquid with a somewhat disagreeable odor. b.p.  $64.7^{\circ}$ . It is a poison and gives rise to blindness when taken internally or applied externally. It burns with a blue flame, quite devoid of soot, to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . On oxidation it first forms the corresponding aldehyde, formaldehyde ( $\text{H}\cdot\text{CHO}$ ), and then formic acid ( $\text{H}\cdot\text{COOH}$ ). The alcohol is used very largely as a solvent in the manufacture of varnishes and lacquers, especially those containing shellac; as a solvent for moving-picture films; in the preparation of denatured alcohol; in the manufacture of formaldehyde; and in the preparation of various dye intermediates.<sup>1</sup> Additional uses are given in the chart facing p. 58.

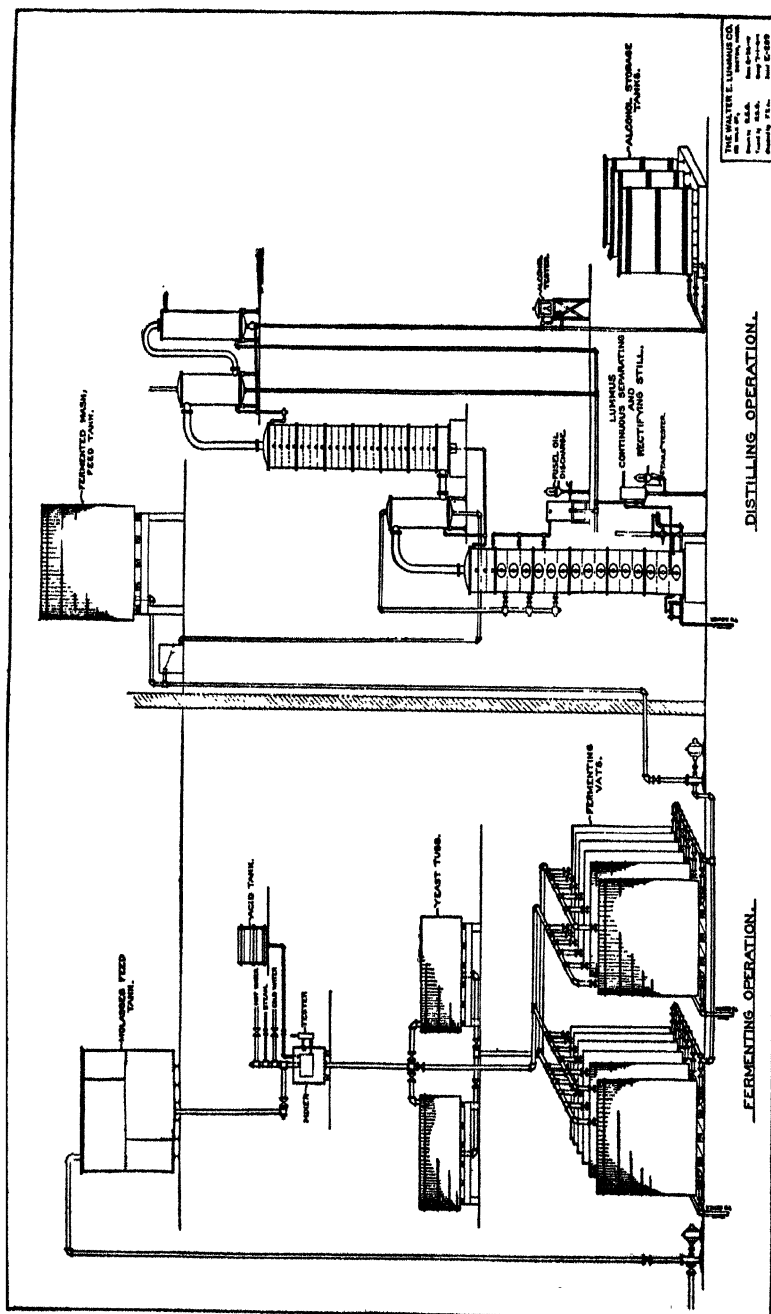
**Ethyl Alcohol**,  $\text{C}_2\text{H}_5\text{OH}$  (also called alcohol, ethanol, grain alcohol, ethyl hydroxide, Cologne spirit and wine spirit). The commercial method of making it is by a process called **fermentation** (fermentation is a process of decomposition brought about by substances secreted by various forms of vegetable and animal life), and in principle differs little from the methods that have been in use for centuries. Some starch-containing substance, such as a cereal (corn, rye, barley, etc.), or potatoes, is allowed to sprout. (The particular raw material used varies in different countries. Sugar and cane molasses from sugar mills are used in the United States; potatoes in Germany; and beet sugar in France.) This develops within the cell a substance known as diastase, a typical catalyst, and called an enzyme because it is produced as a result of cellular activity. The diastase converts the starch to maltose:



Another enzyme, maltase, which is also present, converts the maltose into glucose:

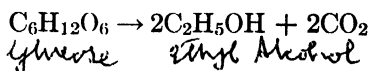


<sup>1</sup> A dye intermediate is an organic compound used in the manufacture of dyestuffs.



THE WALTER E. LUNARUS CO.  
 100 N. 1st St., St. Louis, Mo.  
 Phone 1000  
 Telegrams: W. E. L. Co.  
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Yeast is now added, and the enzyme zymase, present in the yeast, converts the glucose into alcohol and carbon dioxide:



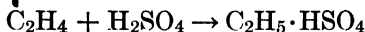
The best temperature for this fermentation ranges from 25–30°.

(Small quantities of impurities, such as glycerol, aldehydes, esters, succinic acid, butyl alcohol, isoamyl alcohol, etc., are also found.) The alcohol in the "wort" (which is the name given to the liquor formed in the course of the fermentation process and which contains from 6–10 per cent of alcohol), is purified by fractional distillation. Commercial ethyl alcohol contains about 95 per cent of alcohol. A still higher percentage of alcohol ("absolute," or nearly 100 per cent alcohol) may be obtained by the addition of calcium oxide (quicklime) or anhydrous copper sulfate (which are dehydrating agents) to the liquid and allowing it to stand a day or two; it is then distilled.

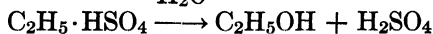
(Such substances as grape juice, corn syrup and molasses are already rich in glucose. Here the preliminary diastase treatment, consisting in the conversion of starch into glucose, is unnecessary.)

A recent process for the preparation of *synthetic ethyl alcohol* involves the following reactions:

*Ethylene*



$\text{H}_2\text{O}$



*Ethyl Hydrogen Sulfate*

**Properties and Uses.**—Ethyl alcohol is a colorless liquid, has a characteristic odor and a sharp burning taste (b.p. 78.4°). In the form of tinctures (alcoholic solutions or extracts of medicinal substances) it is extensively used in medicine. In certain diseases, such as pneumonia, it has proved a valuable therapeutic agent.

The use of alcohol in the industries is very extensive. As a preservative, as an antiseptic, in the preparation of denatured

alcohol and various drugs and medicinals, as a solvent in perfumery, "anti-freeze", as an essential constituent necessary for the manufacture of iodoform, chloroform, vinegar and ether, alcohol is in constant demand. (Additional uses will be found in the chart facing p. 60.)

**Denatured Alcohol.**—This is alcohol which has been made unfit for drinking purposes and external applications, but which can still be used in the industries. Some of the substances used in "denaturing" are methanol, benzine, "alcohol," ether, acetone—substances with disagreeable odors and flavors, and possessing poisonous properties. No less than seventy different formulas have been granted in the United States for the preparation of denatured alcohol for various industrial uses. Denatured alcohol is tax-free.

**Medicated Alcohol** is alcohol unfit for drinking purposes, but suitable for external applications. Some of the substances used in the preparation of medicated alcohol are tartar emetic, formaldehyde, phenol, diethyl phthalate, benzene, acetone, zinc phenolsulfonate, etc.

**Percentages of Alcohol in Beverages.**—Beer=2-5 per cent; wine=7-11 per cent; fortified wine=17-20 per cent; whiskey, brandy, gin, rum, etc.=40-75 per cent.

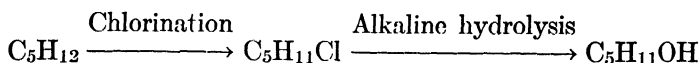
The percentage of alcohol in a number of pharmaceutical preparations is relatively high. Aromatic spirits of ammonia=68 per cent; spirits of camphor=90 per cent; tincture of iodine=83 per cent, etc. For further details consult U. S. Pharmacopeia X.

(Whenever fermented liquors are distilled, not only do we get ethyl alcohol, but also small quantities of esters and a number of the higher alcohols, the mixture of these higher alcohols being substances known as **fusel oil**. Some claim that the presence of fusel oil in liquors is far more harmful than the ethyl alcohol itself. In this connection the following information may be of interest. We know that the principal constituent of fusel oil is

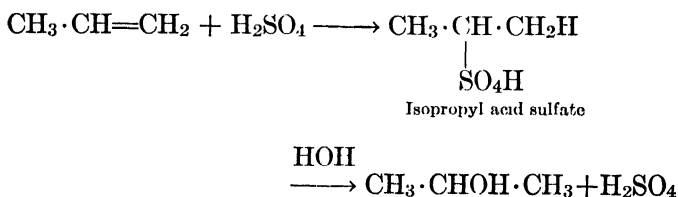
isoamyl alcohol,  $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2\text{OH}$ , and we know that the

source of this is isoleucine, an amino acid obtained from the protein present in cereal or potato (see the chapter on proteins, p. 143. The bacteria present convert the isoleucine into isoamyl

alcohol. It has, however, been shown that this conversion—and hence the production of isoamyl alcohol—may be prevented by the addition of ammonium salts, which the bacteria prefer.) Amyl alcohol is at present manufactured on a commercial scale from the pentane fraction of natural gas by the following series of reactions. †



**Isopropyl alcohol**,  $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CH}_3 \end{array} \begin{array}{c} \text{H} \\ \diagdown \\ \text{OH} \end{array}$ , is made by the reduction of acetone. It is now made by passing propylene gas into sulfuric acid and subsequent hydrolysis:



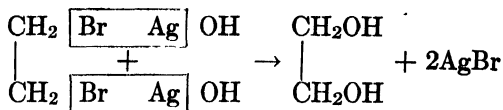
***n*-Butyl alcohol**, *n*-butanol,  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , is produced by the action of bacilli on materials containing starches and carbohydrates (corn) and is used on a large scale as a solvent in the nitrocellulose lacquer industry and for the preparation of esters. **Isoamyl alcohol**,  $\text{C}_5\text{H}_{11}\text{OH}$ , is converted to isoamyl acetate and thus used in the manufacture of varnishes and fruit essences. **Cetyl alcohol**,  $\text{C}_{16}\text{H}_{33}\text{OH}$ , forms (as palmitic ester) the chief constituent of spermaceti (a wax-like substance found in the head of the sperm whale), while **myricyl alcohol**,  $\text{C}_{30}\text{H}_{61}\text{OH}$ , is present as palmitic ester in beeswax and in Carnuba wax. The alcohols are prepared from all these esters by hydrolysis with boiling alcoholic KOH solution.

**Diatomic Alcohols.**—The simplest of these is dihydroxyethane, known as **ethylene glycol**,  $\text{CH}_2\text{OH}$ . It is a compound

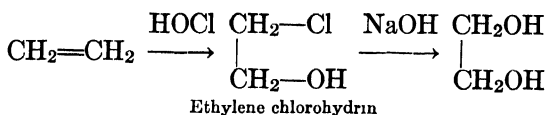


intermediate in composition between ethyl alcohol and glycerol. Its properties are intermediate between these two compounds.

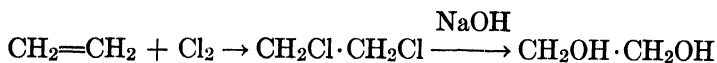
It may be prepared by the action of silver hydroxide on the corresponding dibromo-compound:



but commercially it is made from ethylene:

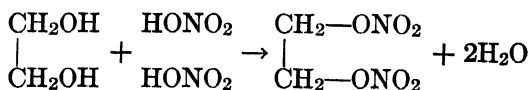


or



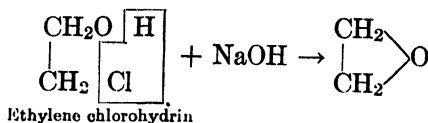
Ethylene glycol is used as a solvent, "anti-freeze" and preservative. The general chemical properties resemble the alcohols, except that we here deal with two OH groups instead of one OH group.

Ethylene glycol combines with  $\text{HNO}_3$  (in the presence of  $\text{H}_2\text{SO}_4$ ) to produce ethylene dinitrate (glycol dinitrate)

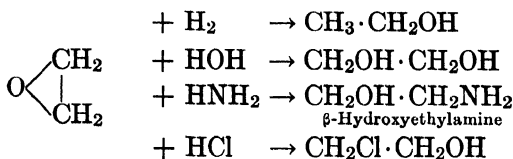


**Ethylene oxide**,  $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array}$ , may be looked upon as an anhydride

of glycol. It is produced by the following reaction.

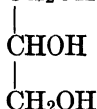


It is a very reactive compound and is used in synthetic organic chemistry.

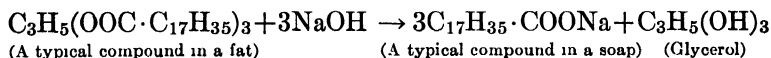


Ethylene oxide is also used in fumigation and as an insecticide.

**Triatomic Alcohols.**—The best known of this group is **glycerol** (also called glycerine),  $\text{CH}_2\text{OH}$  (or 1, 2, 3-propanetriol), which is



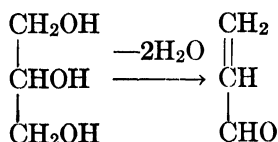
produced as a by-product in the manufacture of soap (p. 99).



(Details of this process will be given in the chapter on esters, p. 99.)

**Properties and Uses.**—Glycerol is a colorless, odorless, syrupy liquid, having a sweetish taste. It is miscible with water and alcohol and is a good solvent and a dehydrating agent. It is used in medicine; as a sweetening agent; as a preservative for tobacco; in perfumery; in cosmetics; in ink for rubber stamps, etc.

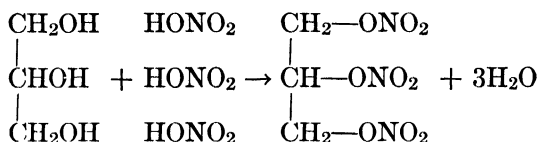
When glycerine is heated alone or in the presence of a dehydrating agent such as  $\text{KHSO}_4$ , **acrolein** is produced:



(The odor of burnt fat is due to the production of acrolein.)

As may be seen from its formula, glycerol is both a primary and a secondary alcohol, and may, therefore, be expected to show the properties of both types of alcohols. When oxidized, aldehydes, acids and ketones are formed. Treatment with acids gives esters. One of the compounds obtained when nitric acid and

glycerol react is of importance; and that is the glyceryl trinitrate or, as it is commonly called, **nitroglycerine**.



(Conc. sulfuric acid is added to remove the water that is formed.) When nitroglycerine explodes the products formed are  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$  and  $\text{N}_2\text{O}$ .

The nitroglycerine is a dangerous explosive to handle, but when mixed with an inert substance, like infusorial earth, “kieselguhr,” thereby becoming **dynamite**, it can be handled with much less risk, though none of its explosive properties are lost. (Starch and sawdust are now used in the place of “kieselguhr,” and oxidizing agents such as ammonium or potassium nitrate are added to aid combustion.)

We owe the invention of dynamite to *Alfred Nobel*, a Swedish engineer, who accumulated a fortune as a result of his invention and who bequeathed it to the Swedish Academy for the purpose of founding the *Nobel Prizes*.

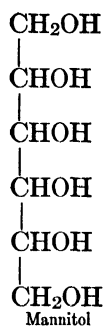
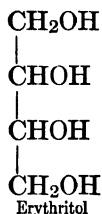
(Vapors of nitroglycerine produce severe headache. In medicine, a 1 per cent solution in alcohol is used. It has a powerful action on the arteries and is used as a heart stimulant.)

Since nitroglycerine freezes in winter and must be thawed before use, it is now being mixed with glycol dinitrate (ethylene dinitrate), which freezes at  $-22.7^\circ$ . Glycol dinitrate is less sensitive to impact than nitroglycerine and is safer to use.

(Glycerol is formed in the digestive tract when the fat in food is hydrolyzed by the enzyme “lipase” of the pancreatic juice. It is also believed that glycerol plays an important part in the oxidation of fats and carbohydrates in the body, for it would seem that one of the intermediate substances formed in such oxidations is glycerol, or a substance very closely allied to it.)

**Polyatomic Alcohols.**—The careful oxidation of the penta- and particularly the hexa-hydroxy alcohols, leads to the compounds known as sugars; but these we shall discuss later. In the meantime, we shall merely mention the names of a few polyatomic alcohols, and write their formulas:





Erythritol occurs in nature, either in the free or combined state, in algae and certain lichens. A source of arabitol is gum arabic. The source of mannitol is the manna ash tree, which, however, is not believed to be related to the "manna" of the Bible. The hexanitrate of mannitol is a high explosive. Dulcitol and sorbitol are isomers of mannitol.

### UNSATURATED ALCOHOLS

$\text{CH}_2=\text{CHOH}$ , ethenol.

$\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{OH}$ , allyl alcohol, or  $\Delta^2$ -1-propenol is present in pyroligneous acid.

(Remember that " $\Delta$ " indicates a "double bond," and that " $\Delta^2$ " indicates double bond in position 2. The ending "ol" in propenol indicates an alcohol, and the "1" before the name means that the OH group is in position 1.)

These compounds possess the general characteristics of alcohols, and being unsaturated compounds, they form additive products with hydrogen, with halogens, with halogen acids, etc.

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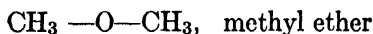
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## CHAPTER VI

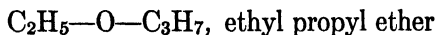
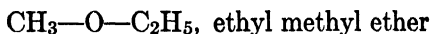
### ETHERS

ETHERS may be considered as derived from alcohols in which the H of the ROH is replaced by an R group; or they may be looked upon as derived from HOH in which both hydrogens are replaced by R groups. The ethers are really organic oxides. (HOH = H<sub>2</sub>O = water = hydrogen oxide; and R—O—R = R<sub>2</sub>O. For example, C<sub>2</sub>H<sub>5</sub>—O—C<sub>2</sub>H<sub>5</sub> = (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O = ethyl oxide, commonly known as "ether.")

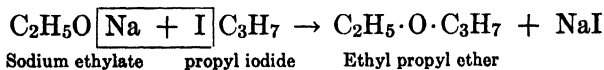
**Types of Ethers.**—If the two R's represent the same groups, then we get a **simple ether**.



If the two R's represent different groups, we get a **mixed ether**.

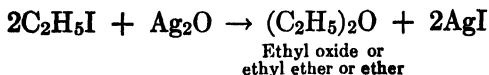


**General Methods of Preparation.**—The action of an alkyl halide on the sodium alcoholate; e.g.,



(This method, the *Williamson's synthesis*, enables one to prepare either a simple or a mixed ether.)

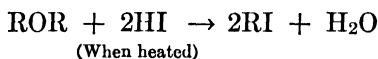
Heating a mixture of silver oxide and alkyl halide; e.g.,



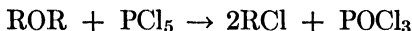
This reaction proves that ether is an oxide.)

**General Properties** —The ethers of low molecular weight are colorless, neutral liquids, more volatile than the corresponding alcohols and lighter than water. They are very stable and inactive, and are therefore used as solvents. The ethers, especially the lower members, are highly flammable.

Sodium, ammonia, alkalies and dilute acids have no action on them. Hydriodic acid acts in one of two ways:



Phosphorus pentachloride has no action in the cold, but when heated,



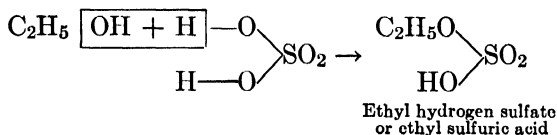
Steam at  $150^\circ$  decomposes them:



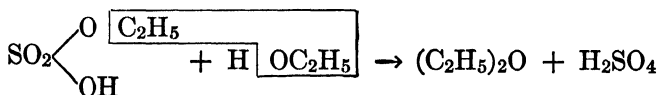
Chlorine replaces the hydrogens in the alkyl groups.

**Ether**,  $\text{C}_2\text{H}_5\text{—O—C}_2\text{H}_5$  (also known as ethyl ether, sulfuric ether and ethyl oxide) is the most important substance of this group.

Ether is manufactured by the “continuous etherification process.” Equimolecular proportions of alcohol and sulfuric acid are mixed:

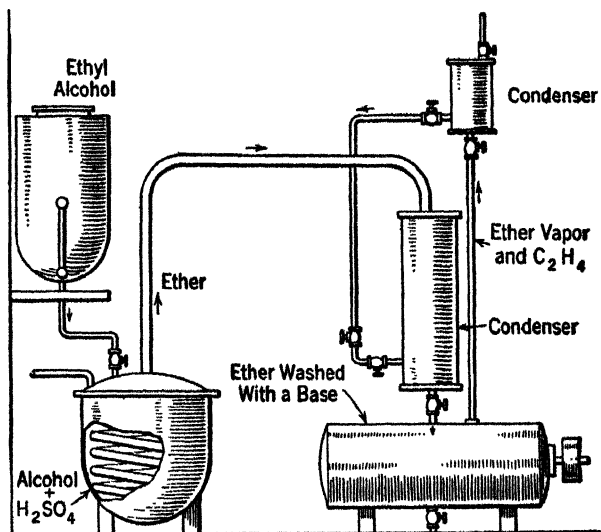
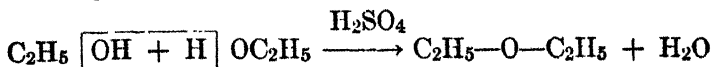


The mixture is now heated to  $130\text{--}140^\circ$  and more alcohol added:



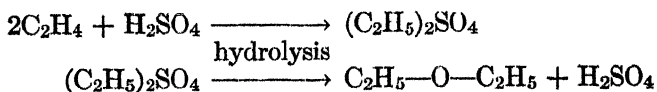
(The sulfuric acid is regenerated and used over again until the acid becomes too weak to react with the alcohol.)

The equation may be expressed:



Manufacture of Ether.

Ether is now also made by the dehydration of two mols. of ethyl alcohol using  $\text{Al}_2\text{O}_3$  as a catalyst (temperature,  $240\text{--}260^\circ$ ). Still another method employs the following reactions:

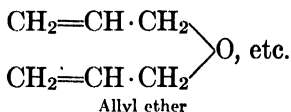
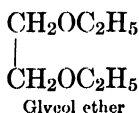


**Properties.**—Ether is a colorless, volatile liquid, with a very characteristic odor. b.p.  $34.6^\circ$ . Specific Gravity = .736 at  $0^\circ$ . It is highly flammable, burning with a luminous flame, and is explosive when mixed with air and ignited. It is slightly soluble in water and is used for extracting certain substances from an aqueous solution. As a solvent for fats, oils, resins, alkaloids, etc., ether is unsurpassed. It can be used as a solvent for quite a number of organic substances. It also dissolves iodine, bromine, sulfur, phosphorus, ferric chloride, etc. It is used with alcohol in the manufacture of guncotton. Due to its rapid evaporation, it can be used for refrigerating purposes. As an anesthetic, it was

introduced in surgery by Dr. Morton, a Boston dentist, in 1846. As an anesthetic, ether is preferred to chloroform, for the physiological effects can be better controlled. Ether for this purpose must be highly purified.

(Ether, chloroform and other anesthetics are, chemically, more or less inert substances and are more soluble in lipoids—typical cell constituents—and lipid solvents than in water.)

### Other Ethers.



The mono ethyl ether of glycol,  $\begin{array}{c} \text{CH}_2\text{OC}_2\text{H}_5 \\ | \\ \text{CH}_2\text{OH} \end{array}$ , is an excellent solvent for cellulose nitrate (p. 182).

For other ethers see chart facing p. 142.

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## CHAPTER VII

### ALDEHYDES AND KETONES

AN aldehyde,  $R \cdot \text{CHO}$ , may be regarded as a hydrocarbon wherein a hydrogen atom has been replaced by the  $\cdot \text{CHO}$  group.

The type formula for an aldehyde is  $R-\text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{H} \end{smallmatrix}$ , and for a ketone,

$\begin{smallmatrix} \text{R} \\ \text{R} \end{smallmatrix} \text{C}=\text{O}$ ; so that a ketone may be regarded as an aldehyde in which the H of the CHO group is replaced by R; and, on the other hand, an aldehyde may be regarded as a ketone in which one of the R groups is replaced by H. Both have the  $\text{>C=O}$

or *carbonyl* grouping, have a number of common properties and they are, therefore, considered in the same chapter. The double bond both in the aldehydes and ketones indicates reactive substances.

(In the chapter on sugars, the student will discover that most of the sugars contain either aldehyde or ketone groupings, and that a number of their properties depend upon these groups; so that much that is gleaned from this chapter can be applied later.)

**Nomenclature of Aldehydes.**—(1) Change the *e* ending of the hydrocarbon having the same number of carbon atoms (or the *ol* ending of the alcohol) to *al*.

$\text{C}_2\text{H}_6$ , ethane —  $\text{C}_2\text{H}_5\text{OH}$ , ethanol —  $\text{CH}_3 \cdot \text{CHO}$ , ethanal

(2) The aldehydes may also be named after the corresponding acids <sup>1</sup> formed when the aldehydes are oxidized.

$\text{H} \cdot \text{COOH}$ , formic acid —  $\text{H} \cdot \text{CHO}$ , formic aldehyde or formaldehyde

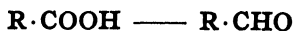
$\text{CH}_3 \cdot \text{COOH}$ , acetic acid —  $\text{CH}_3 \cdot \text{CHO}$ , acetic aldehyde or acetaldehyde

<sup>1</sup> Refer to p. 85.

$C_2H_5 \cdot COOH$ , propionic acid —  $C_2H_5 \cdot CHO$ , propionic aldehyde  
or propionaldehyde

$C_3H_7 \cdot COOH$ , butyric acid —  $C_3H_7 \cdot CHO$ , butyric aldehyde  
or butyraldehyde

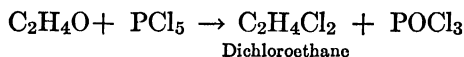
etc.



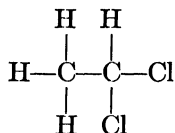
(Never write the group  $\cdot C-OH$  to represent the aldehyde grouping, but always  $\cdot CHO$ . Remember that  $OH$  stands for alcohol and in alcohols the linking is  $R-O-H$  and in aldehydes,  $R-C=O$ .)



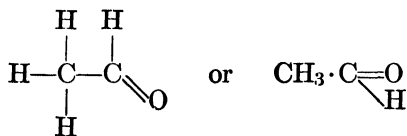
When an aldehyde is treated with phosphorus pentachloride, the reaction is quite different from that obtained when  $PCl_5$  acts on an alcohol. Taking acetaldehyde as an example,



An examination of the dichloroethane reveals that it is the unsymmetrical variety, the two chlorine atoms being attached to the same carbon atom:



which suggests that the oxygen atom in aldehyde occupies a position in the chain corresponding to these two chlorine atoms; that is,



**Nomenclature of Ketones,  $R \cdot CO \cdot R$ .**—(1) Change the *e* ending of the hydrocarbon with the same number of carbon atoms to *one*:

$C_3H_8$ , propane —  $CH_3 \cdot CO \cdot CH_3$ , propanone

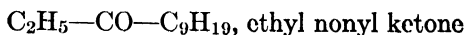
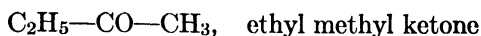
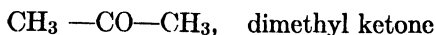
$C_4H_{10}$ , butane —  $CH_3 \cdot CH_2 \cdot CO \cdot CH_3$ , butanone

$C_5H_{12}$ , pentane —  $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_3$ , 2-pentanone  
 $CH_3CH_2COCH_2 \cdot CH_3$ , 3-pentanone

etc.



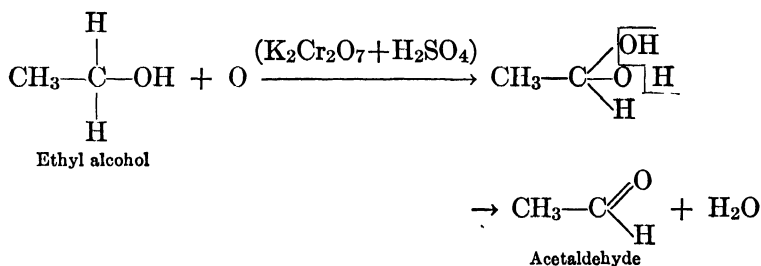
(The type structure for ketone,  $R \cdot CO \cdot R$ , indicates that even the simplest ketone must contain at least three carbon atoms.) (2) Name the compound in accordance with the type of group represented by R, remembering that  $>C=O$  is the ketonic grouping:



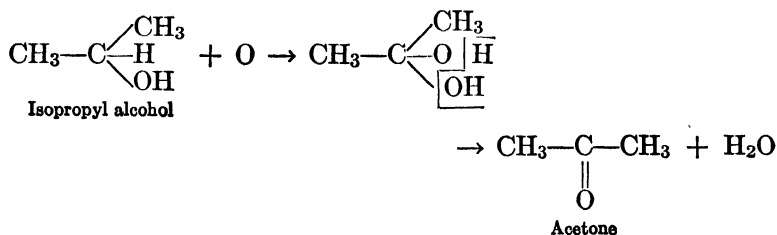
etc.

As with ethers, so with ketones: there are **simple and mixed ketones**. When  $R = R'$  we have a simple ketone; when R is different from  $R'$ , we have a mixed ketone; so that  $C_2H_5 \cdot CO \cdot C_2H_5$  is a simple ketone, and  $C_2H_5 \cdot CO \cdot C_4H_9$  is a mixed ketone.

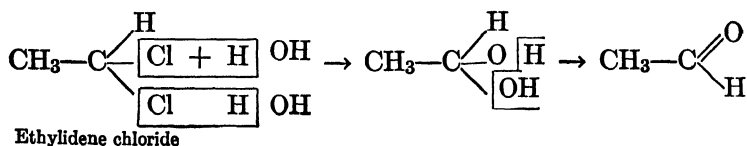
**Preparation of Aldehydes and Ketones.**—The oxidation of a primary alcohol yields an aldehyde; e.g.,



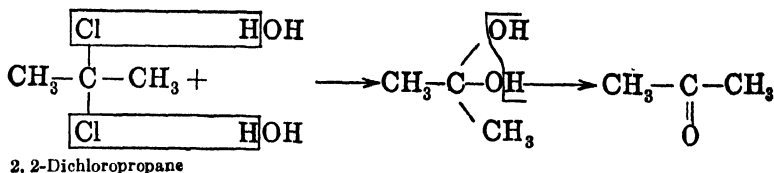
The oxidation of a secondary alcohol yields a ketone; e.g.,



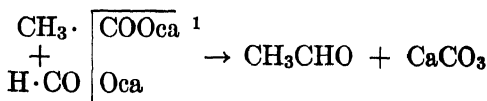
Hydrolysis of dihalogenated hydrocarbons; e.g.,



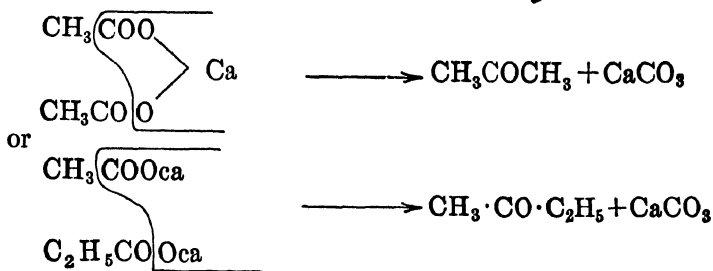
( $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$  is ethylene chloride, but  $\text{CH}_3\cdot\text{CHCl}_2$  is ethylidene chloride.)



Aldehydes may be obtained by heating the calcium salts of certain organic acids with calcium formate; e.g.,



When the calcium salts alone are heated we get ketones; e.g.,



**Chemical Properties of Aldehydes and Ketones.**—We have already mentioned the fact that since both aldehydes and ketones contain the carbonyl,  $\text{C}=\text{O}$  group, they have many properties in common.

The  $\text{C}=\text{O}$  group may be looked upon as an unsaturated group, for it contains a double bond; which means that certain types of addition compounds are possible.

**Acetaldehyde** ( $\text{CH}_3 \cdot \text{CHO}$ ) and **acetone** ( $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3$ ) are here taken as typical examples of aldehydes and ketones respectively.

<sup>1</sup> The true formula for calcium acetate is  $\begin{array}{c} \text{CH}_3 \cdot \text{COO} \\ \text{CH}_3 \cdot \text{COO} \end{array} \text{Ca}$ , but for the sake of convenience we have halved it, and write the symbol for calcium in small letters:  $\text{ca} = \frac{1}{2}\text{Ca}$ .

Reagents Used	Aldehydes, e.g. $\text{CH}_3 \cdot \text{CHO}$	Ketones, e.g., $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3$
Oxidation	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{C}=\text{O} \\   \quad   \\ \text{H} \quad \text{OH} \end{array}$ <p>Acetic acid</p>	<p>→ Decomposition of molecule producing acids with lower carbon content as <math>\text{H} \cdot \text{COOH}</math> and <math>\text{CH}_3 \cdot \text{COOH}</math> and <math>\text{CO}_2 + \text{H}_2\text{O}</math></p>
Reduction	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{OH} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$ <p>A primary alcohol</p>	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{OH} \\   \\ \text{H} \end{array} + \begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{OH} \\   \\ \text{OH} \end{array}$ <p>A secondary alcohol      A pinacol (tetramethyl glycol)</p>
$\text{NaHSO}_3$ Sodium bisulfite	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{OH} \\   \quad   \\ \text{H} \quad \text{OSO}_2\text{Na} \end{array}$ <p>Acetaldehyde sodium hydrogen sulfite</p>	$\begin{array}{c} \text{OH} \\   \\ \text{CH}_3-\text{C}-\text{CH}_3 \\   \\ \text{OSO}_2\text{Na} \end{array}$ <p>Acetone sodium hydrogen sulfite</p>
$\text{NH}_3$	$\begin{array}{c} \text{H} \\   \\ \text{CH}_3-\text{C}-\text{OH} \\   \\ \text{NH}_2 \end{array}$ <p>Acetaldehyde ammonia</p>	<p>Complex condensation products, in place of an addition compound, are formed</p>

HCN	$\begin{array}{c} \text{H} \\   \\ \text{CH}_3 - \text{C} - \text{OH} \\   \\ \text{CN} \end{array}$ <p>Acetaldehyde hydrogen cyanide or ethylidene cyanohydrin</p>	$\begin{array}{c} \text{OH} \\   \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\   \\ \text{CN} \end{array}$ <p>Acetone hydrogen cyanide</p>
PCl <sub>5</sub>	$\begin{array}{c} \text{H} \\   \\ \text{CH}_3 - \text{C} - \text{Cl} \\   \quad   \\ \text{Cl} \quad \text{Cl} \end{array}$ <p>Ethylidene chloride</p>	$\begin{array}{c} \text{Cl} \\   \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\   \\ \text{Cl} \end{array}$ <p>2, 2-Dichloropropane</p>
Halogens	<p>→ substitute in CH<sub>3</sub> group: e.g.,</p> $\begin{array}{c} \text{O} \\    \\ \text{Cl} - \text{C} - \text{CH}_3 \\   \\ \text{Cl} \end{array}$ <p>Trichloroacetaldehyde</p>	<p>→ substitute in CH<sub>3</sub> groups: e.g.,</p> $\text{CCl}_3 \cdot \text{CO} \cdot \text{CH}_3$ <p>Trichloroacetone</p>
H <sub>2</sub> N · OH Hydroxylamine	$\begin{array}{c} \text{H} \\   \\ \text{CH}_3 \cdot \text{C} = \text{O} + \boxed{\text{H}_2} \text{N} \cdot \text{OH} \end{array}$ <p>Acetaldoxime</p>	$\begin{array}{c} \text{CH}_3 \\   \\ \text{C} = \text{O} + \boxed{\text{H}_2} \text{N} \cdot \text{OH} \end{array}$ <p>Acetketoxime</p>
H <sub>2</sub> N · NH <sub>2</sub> Hydrazine or aminoamine	$\begin{array}{c} \text{H} \\   \\ \text{CH}_3 \cdot \text{C} = \text{O} + \boxed{\text{H}_2} \text{N} \cdot \text{NH}_2 \end{array}$ <p>Acetaldehyde hydrazone</p>	$\begin{array}{c} \text{CH}_3 \\   \\ \text{C} = \text{O} + \boxed{\text{H}_2} \text{N} \cdot \text{NH}_2 \end{array}$ <p>Acetone hydrazone</p>

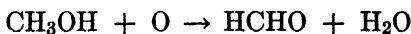
\* The = NOH group is known as the "oxime" group.

Reagents Used	Aldehydes, e.g., $\text{CH}_3 \cdot \text{CHO}$	Ketones, e.g., $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3$
$\text{H}_2\text{N}-\text{NHC}_6\text{H}_5$ † Phenyldiazine	$\text{CH}_3 \cdot \text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{O} + \text{H}_2 \end{array} \text{N} \cdot \text{NHC}_6\text{H}_5 \rightarrow \text{CH}_3 \cdot \text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{O} = \text{N} \cdot \text{NHC}_6\text{H}_5 \end{array}$ <p style="text-align: center;">Acetaldehyde phenylhydrazine</p>	$\text{CH}_3 \cdot \text{C} \begin{array}{l} \text{O} + \text{H}_2 \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \text{N} \cdot \text{NHC}_6\text{H}_5 \rightarrow \text{CH}_3 \cdot \text{C} \begin{array}{l} \text{O} = \text{N} \cdot \text{NHC}_6\text{H}_5 \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$ <p style="text-align: center;">Acetone phenylhydrazine</p>
$\text{C}_2\text{H}_5\text{OH}$ (In presence of a de- hydrating agent, such as $\text{HCl}$ gas)	$\text{CH}_3 \cdot \text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{O} + \text{H} \end{array} \begin{array}{l} \text{H} \\ \diagup \\ \text{OC}_2\text{H}_5 \\ \diagdown \\ \text{OC}_2\text{H}_5 \end{array} \rightarrow \text{CH}_3 \cdot \text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{OC}_2\text{H}_5 \\ \diagdown \\ \text{OC}_2\text{H}_5 \end{array}$ <p style="text-align: center;">Acetal</p>	No similar reaction
	Aldehydes reduce ammoniacal silver nitrate solution to produce silver mirror	Ketones do not

† Phenyldiazine is hydrazine wherein one hydrogen has been replaced by the monovalent  $\text{C}_6\text{H}_5$  (phenyl) group (p 211) The phenyl group bears the same relationship to benzene,  $\text{C}_6\text{H}_6$ , that the methyl group does to methane.

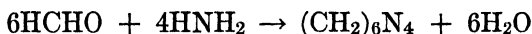
## ALDEHYDES

**Formaldehyde**,  $\text{H} \cdot \text{CHO}$  (also known as methanal) is manufactured by passing methanol vapor and air over copper gauze:



The reaction is exothermic and the copper need not be heated except to start the reaction. It is a gas with irritating odor, soluble in water. The **formalin** of commerce is a 35–40 per cent aqueous solution of the gas. A small amount of methanol must be present in the formalin to prevent the polymerization of the formaldehyde. For disinfecting purposes, specially constructed lamps are used containing methanol, which when burnt (in the presence of copper or platinum) yields formaldehyde. It is used as a food preservative, disinfectant and germicide, both in the form of gas and in solution. In the manufacture of dyes, such as indigo, the hardening of photographic films, the preservation of tissues (hardening the albuminous material), the manufacture of synthetic resins, such as **Bakelite** (see the chapter on phenol, p. 252), formaldehyde finds uses. The chart facing page 80 shows in detail the uses of formaldehyde.

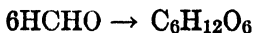
Ammonia and formaldehyde combine to form hexamethylene-tetramine:



commonly known as **urotropine** or “aminoform,” which finds a wide use as a diuretic, urinary antiseptic, liberating formaldehyde; and which is also used in the manufacture of synthetic resins.

It is believed that in the formation of sugars from carbon dioxide and moisture (in the plant kingdom), formaldehyde is an intermediate product. Emil Fischer, the eminent German chemist, has actually been able to obtain a sugar (acrose) from formaldehyde, by treating the latter with barium or calcium hydroxide, thereby forming “formose” (a mixture of sugars), and isolating the acrose from the formose. We shall take this up again in the chapter on sugars.

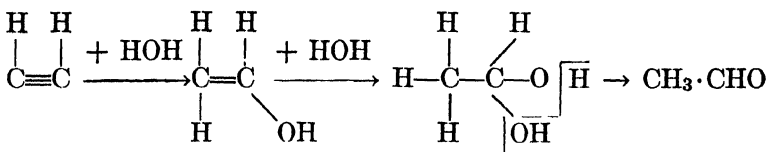
The conversion of formaldehyde into a sugar involves polymerization, and may be represented as



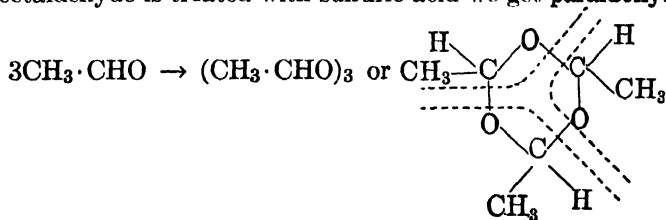
Another polymer of formaldehyde may be obtained by treating the substance with sulfuric acid and evaporating the solution. The paraformaldehyde (also known as “paraform”) so obtained

is a solid and is represented by the formula  $(\text{CH}_2\text{O})_x$ , where  $x$  stands for a number not yet definitely fixed. The formaldehyde gas may again be obtained by simply heating this polymerized formaldehyde. There are lamps on the market which liberate formaldehyde in this way.

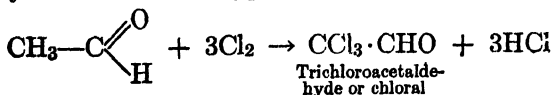
**Acetaldehyde**,  $\text{CH}_3 \cdot \text{CHO}$  (also called ethanal), is manufactured by passing acetylene into dilute  $\text{H}_2\text{SO}_4$  in presence of mercury salts (catalyst). It is probable that what happens may be represented thus:



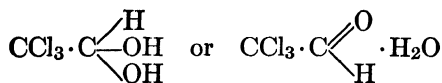
Acetaldehyde may be polymerized, just like formaldehyde. If acetaldehyde is treated with sulfuric acid we get **paraldehyde**:



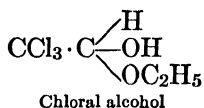
which, since it does not contain the carbonyl ( $>\text{CO}$ ) group, no longer behaves like an aldehyde. If the temperature be lowered (say to  $0^\circ$ ), instead of getting paraldehyde (a liquid), we get an isomeric compound, metaldehyde (a solid), with the same formula. Paraldehyde when heated with dilute acids is converted back to acetaldehyde. (Paraldehyde is used in medicine as a soporific. It is not nearly so volatile and flammable as acetaldehyde, and for this reason acetaldehyde is often transported in the form of paraldehyde and reconverted into acetaldehyde by distillation with dilute acids.) Whereas  $\text{PCl}_5$  reacts with aldehydes, replacing the O of the CHO group by two Cl atoms, chlorine gas displaces the hydrogen atoms in the alkyl part of the molecule; so that, if acetaldehyde be taken as a type, we may get the following:



Chloral is prepared on a large scale from ethyl alcohol (see page 45). Chloral is an oily liquid with a penetrating smell. It reacts with water, forming **chloral hydrate**,

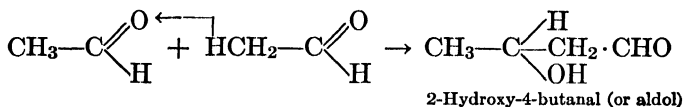


which is used as a soporific. In large doses, it acts as an anesthetic. Chloral also combines with alcohol to form a crystalline body



Bromal,  $\text{CBr}_3 \cdot \text{CHO}$ , and iodal,  $\text{CI}_3 \cdot \text{CHO}$  are also known.

By means of dilute alkali, or a zinc chloride solution, two molecules of acetaldehyde may be made to combine with one another to form aldol, a derivative of butyraldehyde.



This is known as the **aldol condensation**, and, among other things, serves as a working hypothesis to explain the synthesis of fats in the plant kingdom and the conversion of sugars into fats in the animal body.

Higher aldehydes up to  $\text{C}_{22}$  are used in the preparation of synthetic perfumes and artificial fruit flavors.

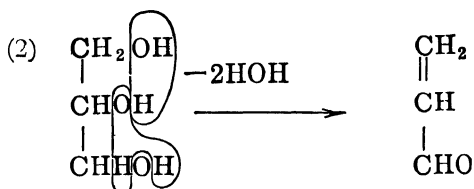
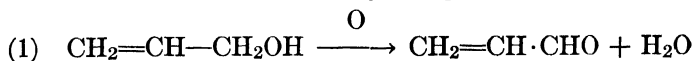
Aldehydes are detected (a) by their reduction of an ammoniacal silver nitrate solution to silver (silver mirror); (b) by the "resin" formation obtained with  $\text{NaOH}$ ; (c) by the formation of a reddish violet color with magenta, which has been decolorized with  $\text{SO}_2$  (the *Schiff* test); (d) by reduction of an alkaline copper sulfate solution (*Fehling's* test), giving the red cuprous oxide.

Glyoxal,  $\begin{array}{c} \text{CHO} \\ | \\ \text{CHO} \end{array}$ , is a dialdehyde. Its dimethyl derivative is dimethyl glyoxal,  $\begin{array}{c} \text{CH}_3 \cdot \text{C}=\text{O} \\ | \\ \text{CH}_3 \cdot \text{C}=\text{O} \end{array}$ , and the dioxime of the latter is



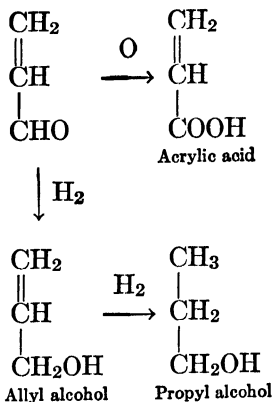
dimethyl glyoxime,  $\begin{array}{c} \text{CH}_3-\text{C}=\text{NOH} \\ | \\ \text{CH}_3-\text{C}=\text{NOH} \end{array}$ , a substance used in the gravimetric determination of nickel.

**Unsaturated Aldehydes.**—Acrylaldehyde,  $\text{CH}_2=\text{CH}-\text{CHO}$ , (commonly called **acrolein**, and sometimes called propenal), is prepared either (1) by the oxidation of allyl alcohol, or (2) by heating glycerol with a dehydrating agent, as  $\text{KHSO}_4$ , or (3) by heating fats and oils to a somewhat high temperature.

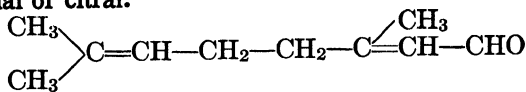


(The odor of burning fat is mainly due to acrolein. Due to its toxic and lachrymatory properties, it was used as a "tear gas" during the late war.)

The properties of acrolein depend, first, upon the fact that it has a double bond (and is, therefore, an unsaturated compound), and second, that it is an aldehyde; so that we get reactions such as these:



**Geranial or citral.**



is found in oil of lemons and citrons.

## KETONES

**Acetone**,  $\text{CH}_3\text{—CO—CH}_3$  (also called propanone and dimethyl ketone) is prepared commercially by heating calcium acetate; by the catalytic dehydrogenation of isopropyl alcohol, and from the products obtained in the fermentation of corn, etc. (Weizmann process.)

This liquid has a characteristic odor, a peppermint-like taste, and is miscible with water. b.p.  $56.1^\circ$ . It is flammable.

Acetone is used in the manufacture of chloroform, iodoform, sulfonal, smokeless powder, celluloid, etc. The chart facing p. 84 shows in detail the uses of acetone.

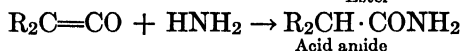
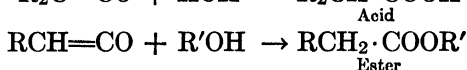
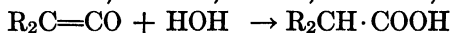
Acetone is an excellent solvent for animal and vegetable oils and for fats, gums, resins, cellulose acetate, nitrocellulose, etc.

Its chemical reactions have already been given (pp. 77–79).

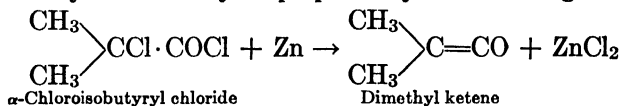
(Acetone is present in the urine and in the breath of persons suffering from severe diabetes.)

Higher ketones up to  $\text{C}_{22}$  are used in the preparation of synthetic perfumes and artificial fruit flavors.

**Ketene** is  $\text{CH}_2=\text{CO}$ . Aldoketenes have the formula  $\text{RCH}=\text{CO}$  and ketoketenes  $\text{R}_2\text{C}=\text{CO}$ . They are very reactive substances. They react with water, alcohols, amines, ammonia, acids, etc.



Dimethyl ketene may be prepared by the following reaction:



$\alpha$ -Chloroisobutyryl chloride

Dimethyl ketene

## READING REFERENCES

- REMLER—Acetone, Its Properties and Uses (National Wood Chemical Association).  
 WALKER—Formaldehyde and Its Polymers. *Industrial and Engineering Chemistry*, **23**, 1220 (1931).  
 KILLEFFER—Butanol and Acetone from Corn. *Industrial and Engineering Chemistry*, **19**, 46 (1927).  
 HOWELLS—Aldol and Related Condensations. *Journal of Chemical Education*, **7**, 597 (1930).  
 CAROTHERS—Polymerization. *Chemical Reviews*, **8**, 353 (1931).

## CHAPTER VIII

### ACIDS

An organic acid contains the "carboxyl" group,<sup>1</sup>

$-\text{COOH}$   $\left( -\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \end{array} \right)$ , and may be regarded as a hydrocarbon

in which one or more of the hydrogens is replaced by COOH groups; e.g.,  $\text{CH}_3\text{H} \longrightarrow \text{CH}_3 \cdot \text{COOH}$ . If the compound contains one COOH group, it is known as a monobasic acid; if two such groups, dibasic; if three, tribasic; etc. We have analogous types in inorganic chemistry; e.g.,  $\text{HCl}-\text{H}_2\text{SO}_4-\text{H}_3\text{PO}_4$ , etc.

**Nomenclature.**—Several acids have names that suggest their origin (formic from "formica," butyric from butter, valeric from "valeriana," palmitic from palm oil, etc.) The acids may also be named by changing the ending *e* of the hydrocarbons containing the same number of carbon atoms, to *oic*; so that

$\text{CH}_4$ , methane becomes  $\text{H} \cdot \text{COOH}$ , methanoic acid

$\text{C}_2\text{H}_6$ , ethane becomes  $\text{CH}_3 \cdot \text{COOH}$ , ethanoic acid

$\text{C}_3\text{H}_8$ , propane becomes  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COOH}$ , propanoic acid

$\text{C}_4\text{H}_{10}$ , butane becomes (a)  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{COOH}$ , butanoic acid

(b)  $\text{CH}_3-\text{C} \begin{array}{l} \nearrow \text{H} \\ \searrow \text{CH}_3 \end{array} \text{COOH}$ , 2-methyl-1-propanoic acid

This type of nomenclature is seldom used.

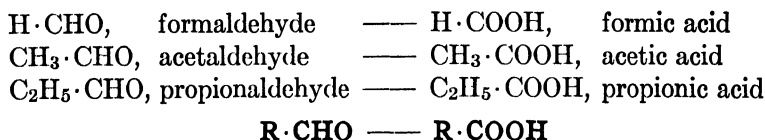
Or they may be named as derivatives of acetic acid,

$\text{CH}_3 \cdot \text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \end{array}$ ; e.g.,

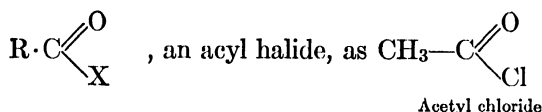
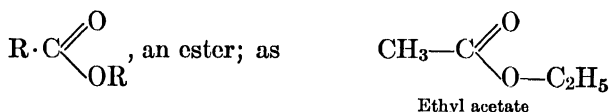
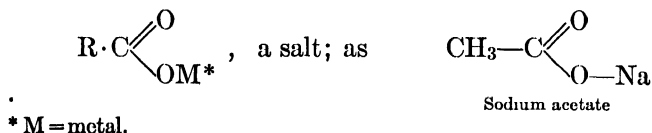
$\text{C}_2\text{H}_5-\text{C} \begin{array}{l} \nearrow \text{H} \\ \searrow \text{CH}_3 \end{array} \text{COOH}$ , ethyl methyl acetic acid

<sup>1</sup> Although other groups, like  $\text{SO}_3\text{H}$ , etc., are also acid groups.

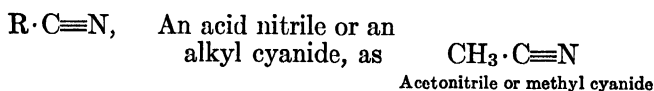
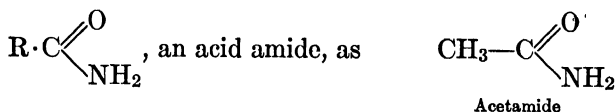
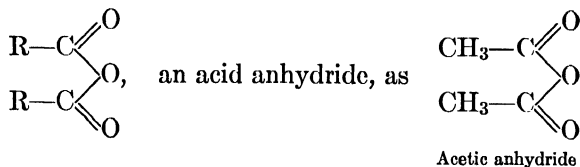
or as the acids of the corresponding aldehydes:



**Types of Acid Derivatives.**—Acids in which some element or group has been substituted in the ·COOH group are called “acid derivatives” (they will be taken up in detail in a later chapter):



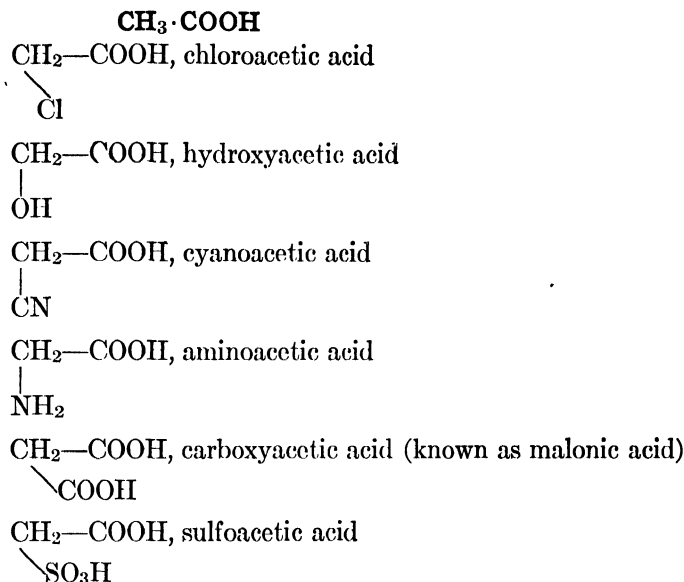
The  $\text{R} - \text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \end{array}$  group is known as the “acyl” group;  $\text{CH}_3 \cdot \text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \end{array}$  group is the acetyl group.



**Types of Substituted Acids.**—Acids in which the ·COOH groups remain, but substitution has taken place in the residual

groups (as  $\text{CH}_3$ ), are known as "substituted acids." (They will be taken up in detail in later chapters.)

Illustration with acetic acid:

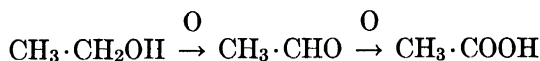


(The  $-\text{SO}_3\text{H}$  group is known as the sulfonic acid group or sulfo group.)

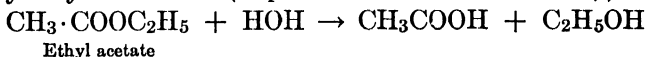
The student should at this point thoroughly familiarize himself with these type compounds, as frequent allusion will be made to them.

#### MONOBASIC ACIDS (FATTY ACID SERIES<sup>1</sup>), $\text{R}-\text{COOH}$

**General Methods of Preparation.**—1. Oxidation of a primary alcohol, or of an aldehyde; e.g.,



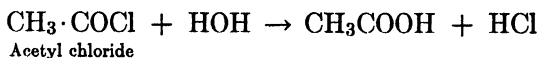
2. Hydrolysis of esters (in presence of acids or alkalis); e.g.,



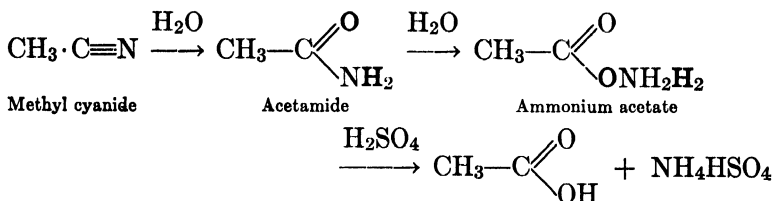
Ethyl acetate

<sup>1</sup> Named **Fatty acids** because many of them are contained in fats, or are formed from fats on hydrolysis.

3. Hydrolysis of acyl halides with water; e.g.,

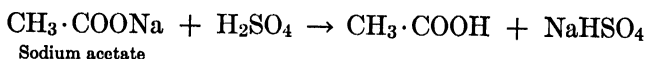


4. Hydrolysis of alkyl cyanides or of acid amides; e.g.,



(—CN group hydrolyzes to a —COOH group.)

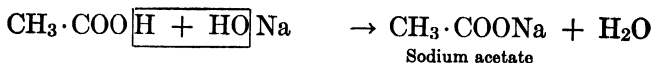
5. Decomposition of salts of organic acids with mineral acids; e.g.,



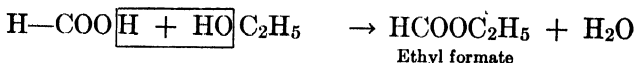
**General Properties.** The lower members up to  $\text{C}_9\text{H}_{19} \cdot \text{COOH}$  are liquids with strong odors, and the higher ones, waxy solids. They ionize to a slight extent (e.g.,  $\text{CH}_3\text{COO}^-\text{H}^+$ ) but their salts ionize quite considerably. They are stable substances and difficult to oxidize.

The acids form:

(a) Salts with bases; e.g.,



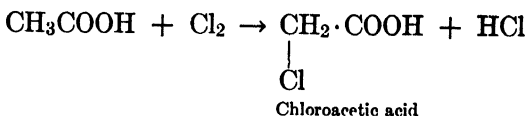
(b) Esters with alcohols; e.g.,



(c) Acyl halides with  $\text{PCl}_5$ ; e.g.,



(d) Halogen substitution products (where halogen substitutes in the alkyl group); e.g.,



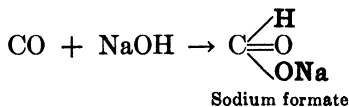
NORMAL FATTY ACIDS \*

Name	Formula
Formic acid.....	H·COOH ✓
Acetic acid.....	CH <sub>3</sub> ·COOH ✓
Propionic acid.....	C <sub>2</sub> H <sub>5</sub> ·COOH
Butyric acid.....	C <sub>3</sub> H <sub>7</sub> ·COOH
Valeric acid.....	C <sub>4</sub> H <sub>9</sub> ·COOH
Caproic acid.....	C <sub>5</sub> H <sub>11</sub> ·COOH
Heptic acid.....	C <sub>6</sub> H <sub>13</sub> ·COOH
Caprylic acid.....	C <sub>7</sub> H <sub>15</sub> ·COOH
Nonylic acid.....	C <sub>8</sub> H <sub>17</sub> ·COOH
Capric acid.....	C <sub>9</sub> H <sub>19</sub> ·COOH
Undecylic acid.....	C <sub>10</sub> H <sub>21</sub> ·COOH
Lauric acid.....	C <sub>11</sub> H <sub>23</sub> ·COOH
.....	.....
.....	.....
.....	.....
.....	C <sub>15</sub> H <sub>31</sub> ·COOH ✓
.....	C <sub>16</sub> H <sub>33</sub> ·COOH
.....	C <sub>17</sub> H <sub>35</sub> ·COOH ✓
.....	C <sub>18</sub> H <sub>39</sub> ·COOH
.....	.....
.....	.....
Melissic acid.....	C <sub>22</sub> H <sub>39</sub> ·COOH

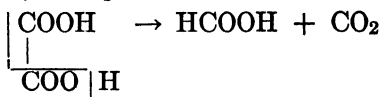
\* For source of these acids, see chapter on them (p. 105)

**Formic Acid**, H—COOH (also known as **methanoic acid**) is a colorless liquid, with an odor resembling sulfur dioxide. It is the strongest acid of this series. It occurs in bees, ants, nettles and pine needles. (The “stinging” by bees is due to penetration of formic acid under the skin.)

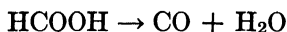
Formic acid is manufactured by heating sodium hydroxide to 150°–170° with carbon monoxide under 6–7 atmospheres of pressure:



In the laboratory, it is prepared by heating oxalic acid with glycerol. The reactions involved are somewhat complex, but the essential feature may be represented thus:

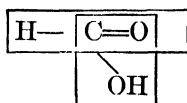


When formic acid is heated with sulfuric acid, we get carbon monoxide and water:



(CO cannot be regarded as the anhydride of HCOOH since CO mixed with water does not give formic acid.)

Formic acid is a reducing agent. This may be explained on the theory that it contains an aldehyde (CHO) as well as an acid (COOH) group:



Formic acid is used in the manufacture of dyestuffs, in dyeing and finishing of textiles, in tanning, etc.

**Acetic Acid.**— $\text{CH}_3 \cdot \text{COOH}$  (ethanoic acid), occurs in fruits and oils in the form of esters. The common form, known as **vinegar**, is produced by the fermentation of fruit juices (such as the apple), which contain sugar. The sugar is first converted to alcohol (due to the presence of the enzyme, zymase), giving us cider, and the latter is oxidized to acetic acid by oxidizing bacteria present in the juice. For large scale production, dilute (6–9 per cent) alcoholic liquor (product of fermentation) is allowed to trickle over beechwood shavings, which are impregnated with “*Bacterium aceti*,” or mother of vinegar. Air is admitted on the side of the vats to oxidize the  $\text{C}_2\text{H}_5\text{OH}$  into  $\text{CH}_3 \cdot \text{COOH}$ . The temperature is kept at about  $35^\circ$ . After the conversion of the alcohol to acetic acid, the product is sold as vinegar.

Vinegar contains from about 3–6 per cent of acetic acid, but also contains other acids (derived from fruit), esters, albuminous matter, etc. Stronger concentration of the acid is obtained from “pyroligneous acid,” which contains acetic acid (4–10 per cent), this being separated from the other constituents of pyroligneous acid by conversion into calcium acetate,  $(\text{CH}_3\text{COO})_2\text{Ca}$  and the subsequent liberation of the acid by the addition of sulfuric acid.

Synthetic acetic acid is now made by the catalytic oxidation of acetaldehyde, which, in turn, is made from acetylene. (See p. 81.)

**Glacial acetic acid** is practically 100 per cent acetic acid, and, as its name implies, resembles ice when frozen.

Acetic acid is used as a solvent and to prepare acetates. It



is also employed in the manufacture of dyes, drugs (like acetanilide, p. 237) and white lead. The chart facing p. 90 shows the extensive uses of acetic acid.

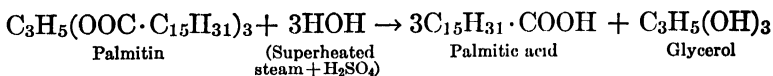
**Propionic Acid.**— $\text{C}_2\text{H}_5\cdot\text{COOH}$ , is present in small amounts in pyroligneous acid.

**Butyric Acid.**— $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , occurs in two forms: as the normal (the formula for which has just been given), and the

iso,  $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \cdot \text{COOH} \\ \diagdown \\ \text{CH}_3 \end{array}$ . The normal variety is present in rancid butter, muscle, sweat, cheese, feces, etc. It has a disagreeable odor. (Calcium *n*-butyrate is one of the few substances more soluble in cold than in hot water.)

**Isovaleric Acid,**  $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \cdot \text{CH}_2 \cdot \text{COOH} \\ \diagdown \\ \text{CH}_3 \end{array}$ , occurs in angelica and valerian roots.

**Palmitic Acid,**  $\text{C}_{15}\text{H}_{31}\cdot\text{COOH}$ , and **stearic acid,**  $\text{C}_{17}\text{H}_{35}\cdot\text{COOH}$  are widely distributed, accompanied by oleic acid,  $\text{C}_{17}\text{H}_{33}\cdot\text{COOH}$ , in most animal and vegetable oils and fats, as the glyceryl esters. (See Chapter X.) From these esters the acids are obtained by hydrolysis; e.g.,



The stearin candles of commerce consist of a mixture of palmitic with excess of stearic acid, and some paraffin added to prevent crystallization and brittleness.

## UNSATURATED MONOBASIC ACIDS

**Acrylic Acid,**  $\text{CH}_2=\text{CH}\cdot\text{COOH}$  (also called propenoic acid) shows characteristic properties due to its double bond and to its carboxyl group.

**Crotonic Acid,**  $\text{CH}_3-\text{CH}=\text{CH}\cdot\text{COOH}$ , derives its name from croton oil.

**Oleic Acid,**  $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ , ( $\text{C}_{17}\text{H}_{33}\cdot\text{COOH}$ ) is present as the glyceryl ester in fats and oils (p. 106), and is usually found associated with palmitic and stearic acids. Oleic acid is a liquid and on a large scale it is separated from the solid

palmitic and stearic acids by squeezing it out under hydraulic pressure. Commercial oleic acid is known as "Red oil" and is used for the manufacture of soap, greases, in the dry-cleaning industry, etc. It is an unsaturated acid, having its double bond between the ninth and tenth carbon atoms. With hydrogen, it is converted into the saturated stearic acid.

**Linoleic Acid**,  $C_{17}H_{31}COOH$ , contains two double bonds. It is present in the form of a glyceryl ester in linseed oil and other drying oils.

### DIBASIC ACIDS, $C_nH_{2n}(COOH)_2$

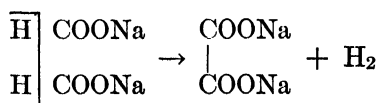
These compounds contain two carboxyl groups. (They are analogous to  $H_2SO_4$ , which contains two replaceable hydrogens.) They are capable of forming two series of salts, viz., acid and normal, and likewise two series of amides, esters, chlorides, etc. The general type reactions are analogous to those given for monobasic acids.

**Oxalic Acid**,  $COOH$ , is present, in the form of salts (potassium,



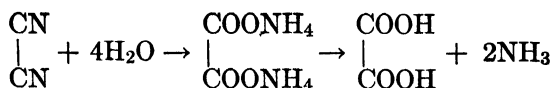
calcium, etc.) in some plants (oxalis variety). Rhubarb is rich in it. The urine often contains small quantities of calcium oxalate.

**Preparation.**—Sugars, cellulose and starch, when oxidized with nitric acid, yield oxalic acid. The commercial method is to heat sawdust with  $NaOH$  at  $240^\circ$ , which yields sodium oxalate. A still more recent method is to heat sodium formate (obtained from carbon monoxide and sodium hydroxide, p. 89) to  $400^\circ$ :

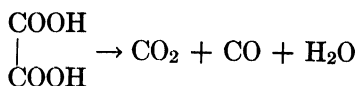


Another method of preparation will be referred to because it is based on a reaction already discussed.

When cyanogen is hydrolyzed, we get oxalic acid:



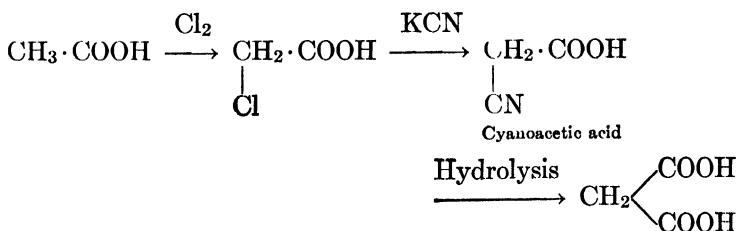
When oxalic acid is heated with sulfuric acid, we get carbon monoxide, carbon dioxide and  $\text{H}_2\text{O}$ :



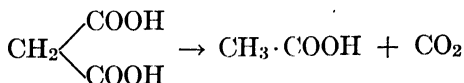
(The student will remember the reaction as a laboratory method for the preparation of CO. The  $\text{CO}_2$  is removed by passing the mixture of gases through alkali.)

Oxalic acid is a highly poisonous substance. It is used in analytical chemistry, in the manufacture of dyes, bleaching, metal polishes, tanning, etc. Oxalic acid is the strongest organic acid.

**Malonic Acid**,  $\text{CH}_2 \begin{array}{l} \nearrow \text{COOH} \\ \searrow \text{COOH} \end{array}$ , was first obtained by oxidizing malic acid (the acid present in apples, p. 131). Its synthesis is accomplished as follows:



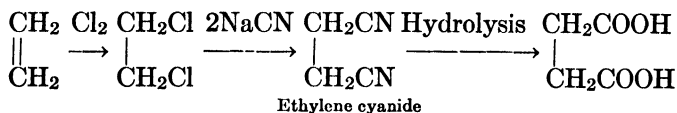
When heated, malonic acid is first converted into acetic acid by the loss of  $\text{CO}_2$ :



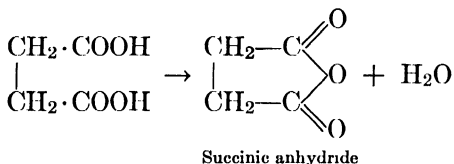
and this proves malonic acid to be a dicarboxylic acid derivative of methane.

**Succinic Acid**,  $\text{CH}_2 \cdot \text{COOH}$ , occurs in amber, fossil wood and  
 $\begin{array}{c} | \\ \text{CH}_2 \cdot \text{COOH} \end{array}$   
 in the urine of animals. It is produced in processes involving

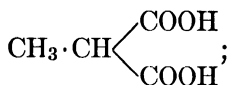
fermentation and may be obtained by distilling amber. Its synthesis may be accomplished thus:



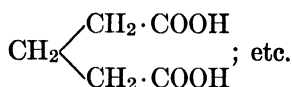
When the acid is heated, it loses a molecule of water and is converted to its anhydride:



Other examples of dibasic acids are methyl malonic acid (isomaleic acid),



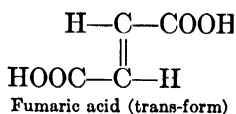
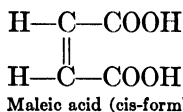
glutaric acid,



### UNSATURATED DIBASIC ACIDS

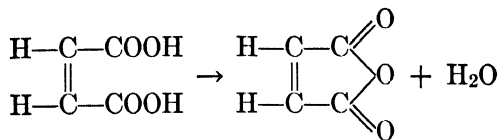
Two compounds with the formula  $\text{C}_2\text{H}_2(\text{COOH})_2$  are known, one being **maleic acid** and the other **fumaric acid**.

Fumaric acid occurs in various fungi, iceland moss, etc. Maleic acid is not a natural product. The formulas ascribed to the two isomers are:



This type of isomerism is known as the "ethylene" or "geometric type,"<sup>1</sup> When maleic acid is heated it produces an anhydride.

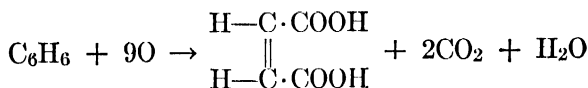
<sup>1</sup> It is suggested that the instructor show this type of isomerism with the Kekulé models.



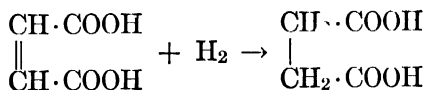
Fumaric acid does not yield an anhydride, which suggests that a compound represented by two  $\cdot\text{COOH}$  groups in juxtaposition has the maleic acid formula.

(The system of nomenclature adopted to distinguish between the two isomers is to term the compound with similar groups on the same side as the *cis*-form, and the compound with similar groups on opposite sides on the molecule as the *trans*-form.)

Maleic acid is prepared on a commercial scale by the catalytic (air) oxidation of benzene vapor:



Both fumaric and maleic acids on reduction yield succinic acid:



### READING REFERENCES

- WEISS AND DOWNS—Catalytic Oxidation of Benzene to Maleic Acid. *Journal of Chemical Education*, **2**, 1178 (1925).  
 CRANOR—Stearic Acid. *Industrial and Engineering Chemistry*, **21**, 719 (1929).  
 PARTRIDGE—Acetic Acid and Cellulose Acetate. *Industrial and Engineering Chemistry*, **23**, 482 (1931).

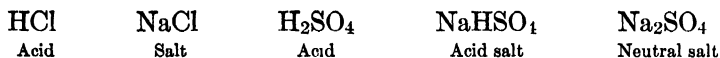
## CHAPTER IX

### SALTS AND ESTERS OF INORGANIC AND ORGANIC ACIDS

#### SALTS

**SALTS** of organic acids are important for a number of reasons. In the first place, they are used in the preparation of various organic compounds (see below); then again a number of them are the source of certain elements which the body needs; and finally a group of them belong to the household substances which go under the common name of "soap."

In inorganic chemistry, a salt may be looked upon as an acid in which the acid hydrogen is replaced by a metal; e.g.,

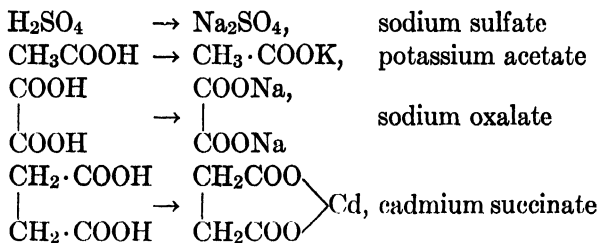


In a similar way, when the acid hydrogen of an organic acid is replaced by a metal, we get a salt:



For example:  $\text{CH}_3\text{COONa}$  (sodium acetate),  $(\text{H} \cdot \text{COO})_2\text{Cu}$  (copper formate),  $\text{C}_{17}\text{H}_{33} \cdot \text{COONa}$  (sodium oleate), etc.

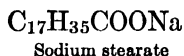
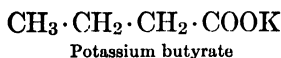
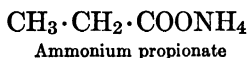
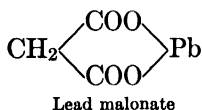
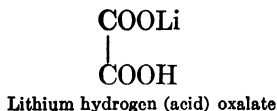
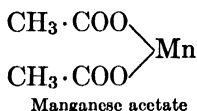
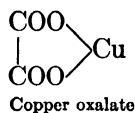
The naming of these salts is analogous to the naming of inorganic salts:



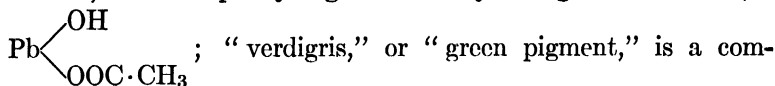
\* M = metal.



Very many salts are known. The names and composition of only a few of these will be given:



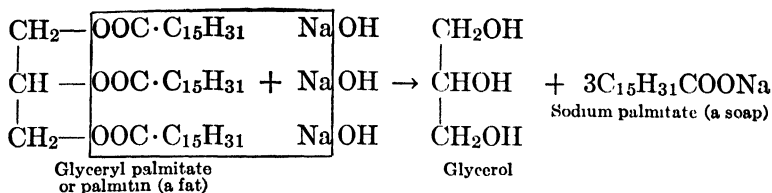
$\begin{array}{c} \text{CH}_3 \cdot \text{COO} \\ \text{CH}_3 \cdot \text{COO} \end{array} \rangle \text{Pb} \cdot 3\text{H}_2\text{O}$  is "sugar of lead"; the "basic lead acetate," used to purify sugar and many biological substances, is



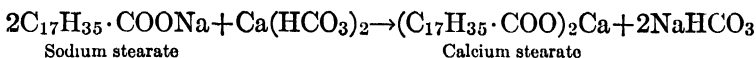
iron, aluminum and chromium acetates are used as mordants in dyeing and calico printing.

**Soaps.**—The sodium or potassium salts of some of the higher acids (obtained from fats and vegetable oils), such as palmitic,  $\text{C}_{15}\text{H}_{31} \cdot \text{COOH}$ ; stearic,  $\text{C}_{17}\text{H}_{35}\text{COOH}$ ; and oleic,  $\text{C}_{17}\text{H}_{33}\text{COOH}$ , are known as **soaps**. Without going into the details of manufacture of these soaps, it may be pointed out that the principle involved is the conversion of the fat into soap and glycerol by boiling with alkali, and the separation of the soap from the glycerol by a process known as "salting out," which means that salt ( $\text{NaCl}$ ) is added to the mixture, whereby the soap comes to the surface and is then ladled off. The reaction may be represented thus:





The solid soaps are sodium salts while the soft soaps are potassium salts. Soaps added to "hard" water (containing calcium or magnesium salts in solution) have their sodium atom replaced by either calcium or magnesium, thereby forming soaps insoluble in water:



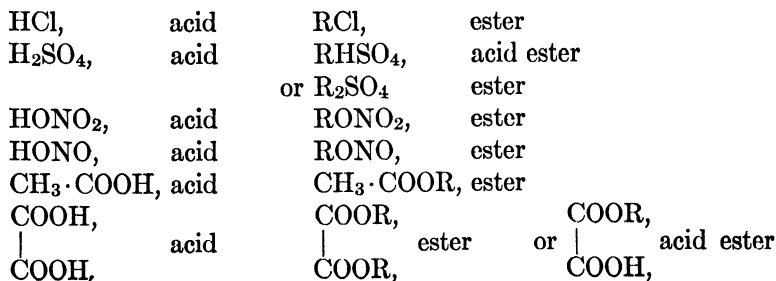
This explains the "curds" formed when soap is used in hard water.

("Lead plaster" is a lead soap made from lead oxide or lead acetate, which has been boiled with fat and water. Lead, manganese or cobalt soaps are used as "dryers" in paints, to hasten the process of drying. Calcium soaps are used for lubricating greases. Zinc stearate finds extensive use in toilet powders. The "medicated" soaps contain one or more of such substances as carbolic acid, salicylic acid, sulfur, cresol, resorcinol, etc. Perfume and coloring materials are often added to soaps.)

The cleansing action of soaps depends upon the power to emulsify oils and fats which are then washed away in the form of small globules.

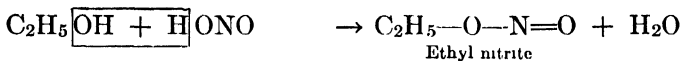
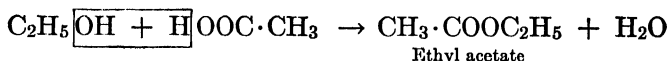
### ESTERS

An **ester** is either an inorganic or organic acid in which the acid hydrogen has been replaced by an R group (or a salt in which the metal is replaced by an R group):

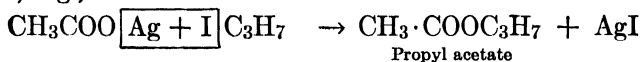


Esters are widely distributed in nature, and are responsible for the characteristic odors of many fruits, flavors and flowers. They have very agreeable odors and are used as flavoring materials and in perfumes. Since they are volatile, the esters are also called "ethereal salts." They ionize to a very slight extent and are usually insoluble in water.

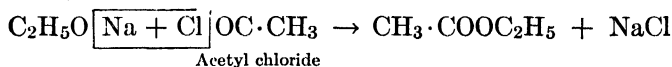
**General Methods of Preparation.**—1. By the interaction of an alcohol and an acid; e.g.,



2. By the interaction of a salt of an acid with an organic halide; e.g.,



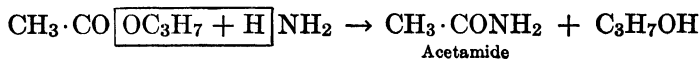
3. The action of an acyl halide on an alcohol or an alcoholate; e.g.,



**General Properties.**—The esters are neutral substances, insoluble in water. Though the salts ionize quite readily, the esters do not. Upon boiling with dilute acid or alkali, hydrolysis takes place, the process being known as **saponification** (a process employed in making soap); e.g.,



Ammonia converts them to the corresponding amide; e.g.,



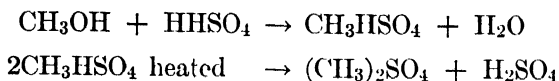
**Esters of Inorganic Acids.**—(The alkyl halides discussed in Chap. IV (p. 44) are esters of hydriodic, hydrobromic and hydrochloric acids. They will not be discussed again in this section.)

**Ethyl nitrite**,  $\text{C}_2\text{H}_5\cdot\text{ONO}$ , has an apple-like odor. Its alcoholic solution is the "sweet spirit of nitre." **Isoamyl nitrite**,

$C_5H_{11} \cdot ONO$ , is used in medicine as an antispasmodic and anodyne.

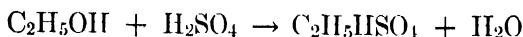
**Ethyl nitrate**,  $C_2H_5ONO_2$ , has a fruity odor. It is explosive.

**Dimethyl sulfate**,  $(CH_3)_2SO_4$ , may be prepared thus:



It finds use as a methylating agent (to introduce methyl groups into compounds). It is poisonous.

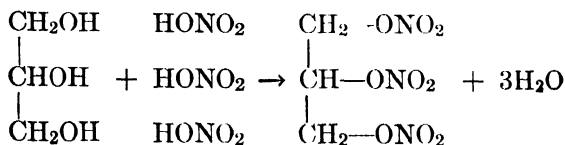
**Ethyl sulfuric acid**,  $C_2H_5HSO_4$  (also called **ethyl hydrogen sulfate**), may be prepared by the action of conc. sulfuric acid on ethyl alcohol at  $100^\circ$ :



It may be recalled at this point that when ethyl hydrogen sulfate is heated to about  $170^\circ$  we get ethylene (p. 32) and when treated with alcohol it yields ether (p. 70).

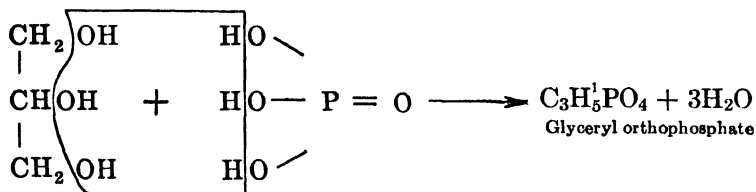
**Diethyl sulfate**,  $(C_2H_5)_2SO_4$ , is used as an ethylating agent. It has a peppermint-like odor. Unlike dimethyl sulfate, it is non-toxic.

**Glyceryl trinitrate**, commonly, but erroneously, called **nitroglycerine**, is prepared by the action of nitric acid on glycerine ( $H_2SO_4$  is used as dehydrating agent):



It is used in medicine as a circulatory depressant and is the active constituent of dynamite (see p. 66).

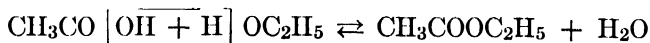
**Glyceryl phosphate** (ortho) is prepared in a similar manner:



<sup>1</sup> The  $C_3H_5$  group, if trivalent, is known as the glyceryl group; if  $C_3H_5$  is monovalent, it is known as the allyl group.

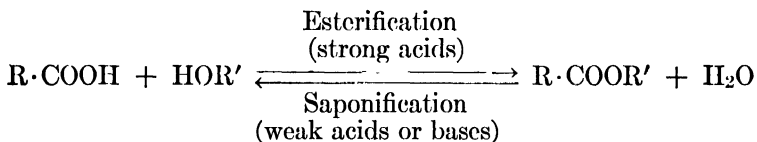
(RCN may be regarded as an ester of HCN. This type of compound will be treated later—p. 161).

**Esters of Organic Acids.**—When an inorganic acid and an alkali react, a salt is immediately formed; when, however, an organic acid and an alcohol (in some respects the analogue of the alkali) react, the ester is formed, but slowly:



When equimolecular quantities are used, only 66 per cent of the ester is produced. An increase of temperature increases the velocity of the reaction, but not the yield of ester. The latter may be increased by the addition of a catalyst, or a dehydrating agent, such as  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  gas.

**Saponification** to which we have alluded (p. 100) is hydrolysis, and **esterification** is the reverse of this:



Many of these esters are known. They are used extensively in artificial fruit essences, flavors, perfumes, extracts, etc. Very many soft drinks on the market are artificially colored and flavored. Synthetic esters are used to flavor them and a number of coal-tar dyes to color them. Only a few can be mentioned here.

**Ethyl acetate**,  $\text{CH}_3 \cdot \text{COOC}_2\text{H}_5$ , is used as a solvent for nitro-cellulose, in the preparation of photographic films, and in resins and essences.

**Isoamyl acetate**,  $\text{CH}_3 \cdot \text{COOC}_5\text{H}_{11}$ , is found in pear oil and is used as a solvent for gun-cotton and in the preparation of banana oil or "bronzing" liquid.

**Ethyl butyrate**,  $\text{C}_3\text{H}_7 \cdot \text{COOC}_2\text{H}_5$ , is a constituent of pine-apples.

**Isoamyl isovalerate**,  $\text{C}_4\text{H}_9 \cdot \text{COOC}_5\text{H}_{11}$ , is found in apples.

**Octyl acetate**,  $\text{CH}_3 \cdot \text{COOC}_8\text{H}_{17}$ , occurs in oranges.

**Ethyl formate**,  $\text{H} \cdot \text{COOC}_2\text{H}_5$ , is a constituent of artificial rum.

**Amyl butyrate**,  $\text{C}_3\text{H}_7 \cdot \text{COOC}_5\text{H}_{11}$ , has an apricot flavor.

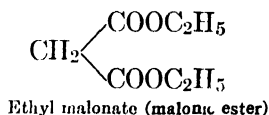
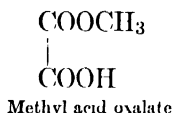
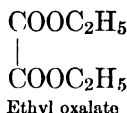
**Ethylene acetate**,  $\text{CH}_3 \cdot \text{COOCH}_2$ , is used as solvent for cellu-



lose acetate and in cellulose nitrate lacquers.

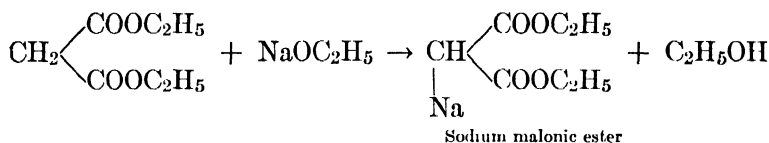
As a result of the development of the lacquer industry during the last few years, many of these esters are now finding extensive use.

**Myricyl palmitate**,  $\text{C}_{15}\text{H}_{31} \cdot \text{COOC}_{30}\text{H}_{61}$ , is present in beeswax. The esters of dibasic acids are also well known; e.g.,

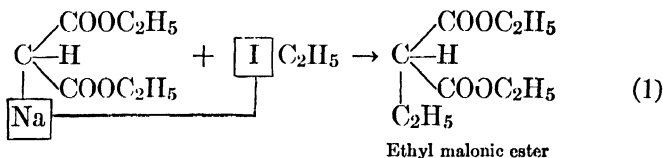


**Uses of Malonic Ester.**—Malonic ester can be used to synthesize homologues of malonic and acetic acids.

When malonic ester is treated with sodium or sodium alcoholate, the following reaction takes place:

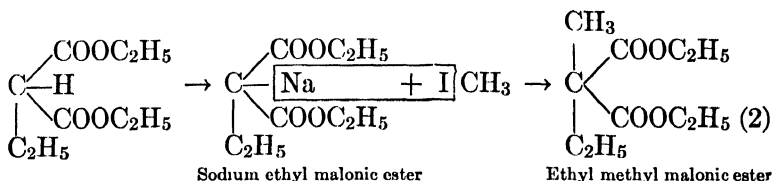


If an alkyl halide is now added; e.g.,

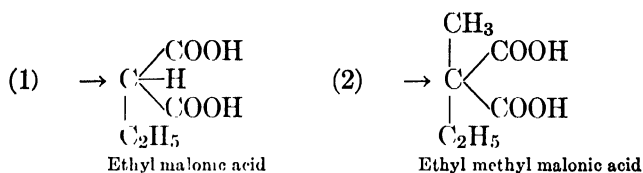


a derivative of malonic ester is obtained.

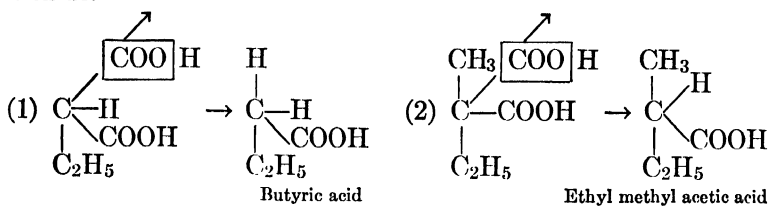
A second alkyl group (the same or a different one) may be introduced by repeating the above operation; e.g.,



On hydrolysis with sodium hydroxide and subsequent acidification the following acids are formed:



On heating, malonic acid and its derivatives lose carbon dioxide.



(**Fats** and **vegetable oils** are glyceryl esters. They will be taken up in detail in the next chapter.)

### READING REFERENCES

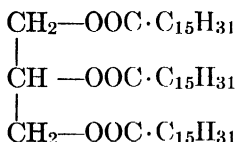
- ROGERS—Manual of Industrial Chemistry. (1931), p. 1003 (Soaps and Soap Products).  
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# CHAPTER X

## FATS AND OILS, WAXES AND LIPOIDS

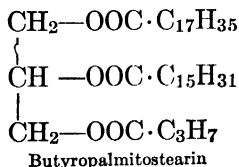
### FATS AND OILS

THESE are glyceryl esters of fatty acids (usually of high molecular weight). An example of one of these substances is glyceryl palmitate (tripalmitin).



The glyceryl esters of stearic ( $\text{C}_{17}\text{H}_{35}\text{COOH}$ ), palmitic and oleic ( $\text{C}_{17}\text{H}_{33}\text{COOH}$ ) acids constitute the main bulk of the fats and oils in food and of body fat.

If the three acid radicals in a fat or oil are the same, it is known as a simple glyceride, e.g., tripalmitin. A fat containing radicals of two or three different fatty acids is known as a mixed glyceride, e.g.,



There is no essential chemical difference between fats and vegetable oils. **Stearin**,  $\text{C}_3\text{H}_5(\text{OOC}\cdot\text{C}_{17}\text{H}_{35})_3$ , and **palmitin**,  $\text{C}_3\text{H}_5(\text{OOC}\cdot\text{C}_{15}\text{H}_{31})_3$  are solids, while **olein**,  $\text{C}_3\text{H}_5(\text{OOC}\cdot\text{C}_{17}\text{H}_{33})_3$  is a liquid. The consistency of a fat or oil depends on the amount of solid or liquid esters present. The fats are solid at the ordinary temperatures, whereas the oils are liquid.

## IMPORTANT FATS AND OILS

Fat or Oil	Contains the Glyceryl Ester of	Source of Fat or Oil
Almond oil	Oleic, palmitic, linoleic acids, etc.	Bitter or sweet almonds
Butterfat	Butyric, caproic, capric, palmitic, stearic, oleic acids, etc.	Cow's milk
Cacao butter	Palmitic, oleic, stearic, myristic acids, etc.	Seeds of cocoa nibs
Castor oil	Ricinoleic, stearic, oleic acids, etc.	Seeds of castor beans
Cocoonut oil	Caproic, caprylic, capric, lauric acids, etc.	Seeds of "cocos nucifers," kernel of nuts
Codliver oil	Oleic, myristic, palmitic, stearic acids and cholesterin, etc.	Livers of cod fish
Cottonseed oil	Oleic, stearic, palmitic, linoleic acids, etc.	Seeds of the cotton-plant
Hemp oil	Isolinolenic, oleic acids, etc.	Seeds of hemp
Human fat	Stearic, palmitic, oleic, butyric, caproic acids, etc.	Human beings
Lard	Stearic, palmitic, oleic, linoleic acids, etc.	Body fat of swine
Linseed oil	Linoleic, linolenic, oleic, palmitic, myristic acids, etc.	Seeds of flax
Maize oil	Arachidic, stearic, palmitic, oleic acids, etc.	Seed germs of corn oil
Menhaden oil	Palmitic, myristic, oleic, stearic, and other unsaturated acids, etc.	Bodies of menhaden fish
Mustard oil	Erucic, arachidic, stearic, oleic acids, etc.	Seeds of mustard
Neatsfoot oil	Palmitic, stearic, oleic acids, etc.	Hoofs of cattle
Olive oil	Linoleic, oleic, arachidic acids, etc.	Fruit of olive tree

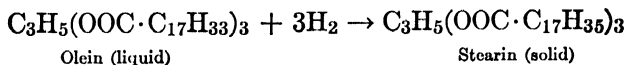


IMPORTANT FATS AND OILS—*Continued*

Fat or Oil	Contains the Glyceryl Ester of	Source of Fat or Oil
Palm oil	Palmitic, lauric, oleic acids, etc.	Palm seed
Peanut oil	Arachidic, linoleic, hypogoeic, palmitic acids, etc.	Peanuts
Poppy oil	Linoleic, isolinolenic, palmitic, stearic acids, etc.	Poppy seeds
Rape oil	Erucic, arachidic, stearic acids, etc.	Rape seeds
Sperm oil	Oleic, palmitic acids, waxes, etc.	Head and blubber of sperm whale
Tallow	Stearic, palmitic, oleic acids, etc.	Fat of ox or sheep
Whale oil	Linoleic, isolinolenic acids, etc.	Blubber of whales

**Oleomargarine** consists mainly of refined lard, "oleo oil" (the soft part of beef fat) and cottonseed oil, often mixed with a small amount of butter and churned with milk or cream.

**Hydrogenation of Oils.**—Liquid fatty oils can be converted to fatty bodies of almost any desired degree of consistency by means of hydrogenation. The unsaturated liquid oils unite directly with hydrogen in presence of catalysts (nickel being used on commercial scale) to form saturated bodies.

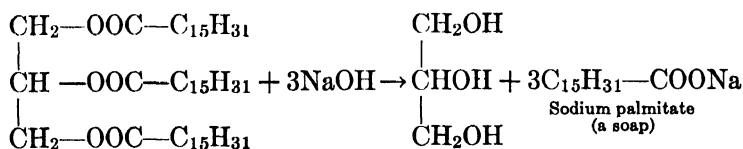


Stearin has greater commercial value than olein. The "hardened fats" now find extensive use in the preparation of lard substitutes, in the manufacture of soap, etc. "Hardened" cottonseed oil, peanut oil and other edible oils have largely replaced lard compounds. "Crisco," "vegetol," are examples of "hardened" (or hydrogenated) vegetable oils.

Crude fats and oils range from yellow to red in color. The

refined products are generally yellow to colorless. Sometimes vegetable oils are green, due to the presence of chlorophyll (the green coloring matter of plants). Fats and oils are insoluble in water, but readily soluble in ether, benzene, chloroform, etc. The rancidity of a fat (as in butter-fat) is mainly due to hydrolysis (bacterial decomposition, or otherwise) and oxidation yielding the free fatty acids. Butter in this way produces butyric acid, which has a disagreeable odor.

**Properties.**—Fats can be hydrolyzed or saponified. When the glyceryl esters of stearic, palmitic or oleic acids are saponified with NaOH or KOH, soaps are formed:



This is the principle employed in the manufacture of soap. (The reaction also explains the hydrolysis of fats in the small intestine by the enzyme (lipase) which is formed in the pancreas.)

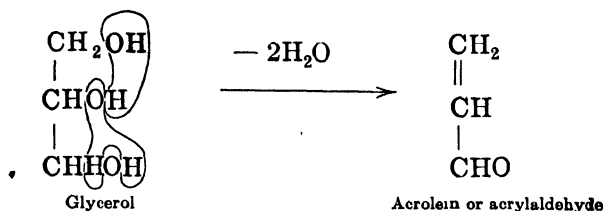
A number of methods used for identifying fats are:

1. Saponification value: the number of milligrams of KOH needed to saponify 1 gram of fat or oil.
2. The iodine number: the percentage of iodine absorbed by the sample. (The amount of "absorption," or extent of "addition" will depend upon the amount of unsaturated glycerides present—such as in olein, for example.)
3. Specific gravity.
4. Melting point.
5. Index of refraction.
6. Viscosity and other physical constants.

(As has been stated, the fats in the body are first hydrolyzed into fatty acids and glycerol. A little soap is also formed, due to the alkalinity of the medium. The fatty acids and glycerol are absorbed as such through the lining of the small intestine, where they are re-synthesized again into fat, most of which passes into the lymphatic system, and finally finds its way into the blood stream. Some of the fat is oxidized in the cells, to  $\text{CO}_2$  and water—see the steps in this oxidation p. 189—but much of it

is often deposited in the adipose tissue, and acts as a reserve fuel.)

The fats and oils, when strongly heated, either alone, or with a dehydrating agent like  $\text{KHSO}_4$ , develop a penetrating odor, due to the formation of acrolein. This acrolein is really derived from the glycerol part of the molecule:



### WAXES

**Waxes**, like fats, are esters, but instead of containing the trihydroxy alcohol, glycerol, they contain high molecular weight monatomic alcohols, such as cetyl alcohol,  $\text{C}_{16}\text{H}_{33}\text{OH}$ , carnaubyl alcohol,  $\text{C}_{24}\text{H}_{49}\text{OH}$ , myricyl alcohol,  $\text{C}_{30}\text{H}_{61}\text{OH}$ , etc.

Among vegetable waxes, we have "carnauba wax," and among animal waxes, we have wool wax (or "lanolin"), beeswax, spermaceti, Chinese insect wax, etc.

Waxes (like fats) are soluble in ether, benzene, chloroform, carbon tetrachloride, etc. Since they do not contain glyceryl radical, they do not yield acrolein when heated. The waxes do not become rancid like fats and are less easily hydrolyzed.

Carnauba wax is derived from a species of palm; it is used in varnish, for candle making and for adulterating beeswax. Lanolin, obtained from wool grease, is used in pharmacy as a basis for salves, ointments and emulsions. Beeswax is derived from the honeycomb of bees and is used in candle making, in pharmacy, etc. Spermaceti, found in the head of the sperm whale, finds uses in candle making, in pharmacy and in confectionery. Chinese wax, secreted by an insect, is also used in candle making, in medicine and as a furniture polish, etc.

## LIPOIDS

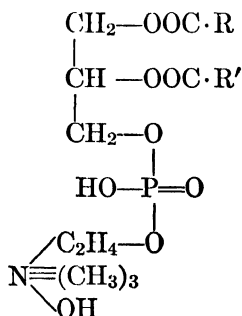
These are a group of substances, soluble in ether and the usual fat solvents, which are found in abundance in animal tissues, particularly in the brain. We know little at present about their physiological significance. They may be classified as follows:

1. Containing nitrogen and phosphorus (phosphatids); e.g., lecithin and cephalin (N : P as 1 : 1), and sphingomyelin (here N : P as 2 : 1).

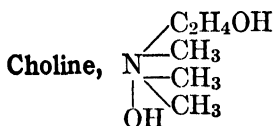
2. Containing nitrogen: e.g., phrenosin and cerasin (the so-called "cerebrins" or "cerebrosides").

3. Nitrogen and phosphorus are absent; e.g., cholesterol.

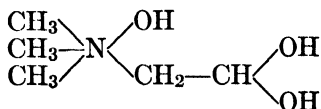
**Lecithin** is a combination of glycerol, fatty acid, phosphoric acid and choline, and its structure may be represented as:



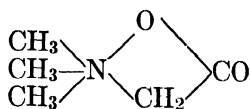
(R and R' represent groups present in acids. As in fats, R and R' may be the same or different.)



or trimethyl- $\beta$ -hydroxyethyl ammonium hydroxide, is closely related to **muscarine**—the aldehyde hydrate of choline—

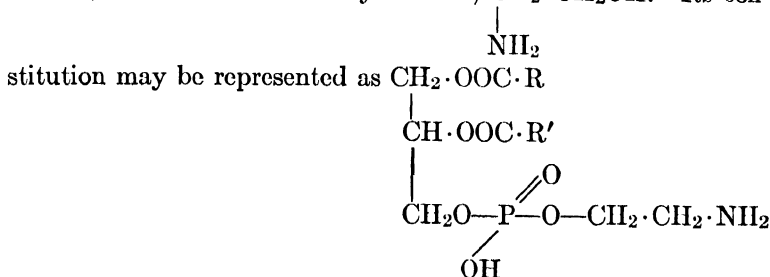


which is the poisonous constituent of the deadly toad-stool, and to **betaine**—the acid anhydride—



a non-toxic plant product. In a crude form, lecithin may be obtained by extracting egg yolk with ether and precipitating with acetone.

**Cephalin** is similar to lecithin in that it contains glycerol, fatty acids and phosphoric acid, but in the place of the base choline, it contains aminoethyl alcohol,  $\text{CH}_2 \cdot \text{CH}_2\text{OH}$ . Its con-



Unlike lecithin, cephalin is insoluble in alcohol. (Cephalin is sometimes written “kephalin.”)

**Sphingomyelin** is a complex combination of phosphoric acid, choline, a base, sphingosine,  $\text{C}_{17}\text{H}_{32}(\text{OH})\text{NH}_2$ , and an acid, lignoceric acid,  $\text{C}_{25}\text{H}_{47} \cdot \text{COOH}$ .

**Phrenosin** is a combination of cerebronic acid (the hydroxy acid of lignoceric), galactose and sphingosine.

**Cerasin**, like phrenosin, yields when hydrolyzed, galactose and sphingosine, but in the place of cerebronic acid gives lignoceric acid.

**Cholesterol**,  $\text{C}_{27}\text{H}_{45}\text{OH}$ , is an unsaturated secondary alcohol and a member of the terpene series, though its exact structure is not yet known. It is widely distributed in animal tissues, particularly in egg yolk and nervous tissue. (Isomers, **phytosterols**, are found in the vegetable kingdom.) “Lanolin,” the fatty matter obtained from sheep’s wool, is an ester of cholesterol. This alcohol is also present in bile and in blood. The determination of the amount of cholesterol in the blood is often of chemical

significance, since in gall stones, pregnancy, nephritis, diabetes, etc., the quantity may be in excess of the normal value.

Recently it has been shown by Hess and Steenbock that ultra-violet rays convert ergosterol into a substance showing antirachitic properties, a characteristic usually ascribed to vitamin D (p. 359). It is now believed that the precursor of vitamin D is probably this ergosterol,  $C_{27}H_{41}OH$ .

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## CHAPTER XI

### ACID ANHYDRIDES, ACYL HALIDES AND ACID AMIDES

The type formula for an acid anhydride is

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$$

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$$

The type formula for an acyl halide is

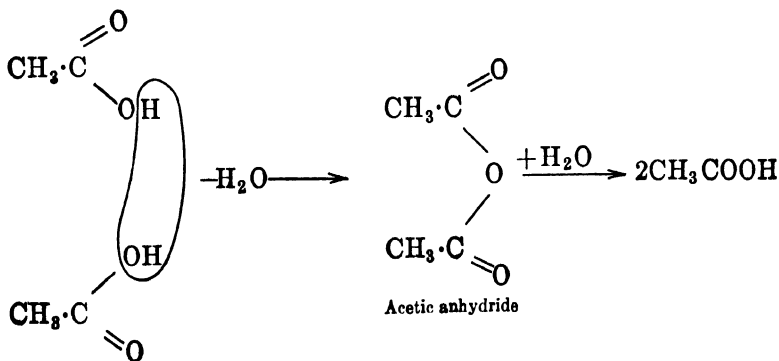
$$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \diagdown \quad \diagup \\ \text{X} \end{array}$$

The type formula for an acid amide is

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \diagdown \quad \diagup \\ \text{NH}_2 \end{array}$$

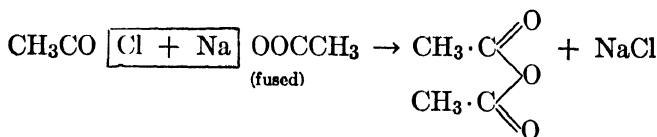
#### ACID ANHYDRIDES

Acid anhydrides are similar in many respects to inorganic acid anhydrides. Sulfur trioxide, for example, is the acid anhydride of sulfuric acid, for  $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ . Similarly, acetic (acid) anhydride is the anhydride of acetic acid, for



(An anhydride may be looked upon as an acyl oxide.)

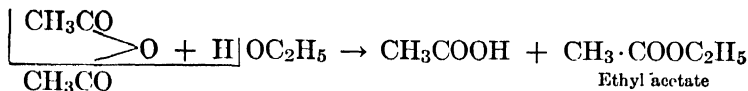
**General Methods of Preparation.**—1. By heating an acyl halide and the salt of an acid, e.g.,



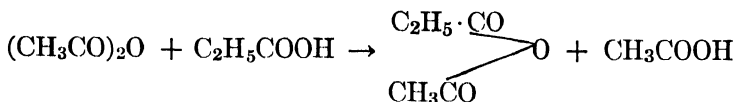
2. By the action of a dehydrating agent (such as  $\text{P}_2\text{O}_5$ ) on the acid. Acetic anhydride may in this way be prepared from glacial acetic acid. However, the yield is poor.

**Acetic anhydride** is the most important member of the series and the general properties of these anhydrides can be illustrated by summarizing the properties of acetic anhydride. (Formic anhydride is not known.)

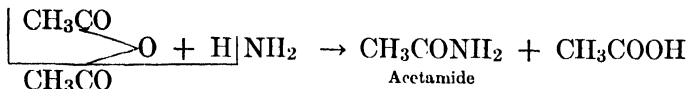
It has already been mentioned that acetic anhydride reacts with water to form acetic acid. With alcohol, a mixture of acid and ester is formed:



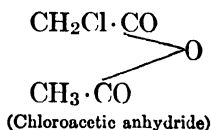
With propionic acid, a mixed anhydride is obtained:



With ammonia, the corresponding amide is formed:



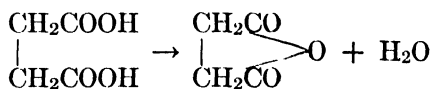
Chlorine and bromine yield substituted anhydrides; e.g.,



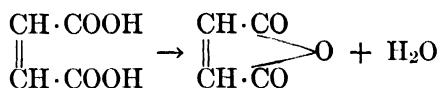
Acetic anhydride is a liquid with a pungent, suffocating odor. It finds extensive use as a means of introducing the  $\text{CH}_3\text{CO}$  (acetyl) group into compounds (for example, cellulose acetate.)



**Succinic anhydride** may be obtained by heating succinic acid:



Similarly **maleic anhydride** may be obtained from maleic acid:

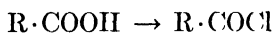


The properties of these compounds are analogous to acetic anhydride

### ACYL HALIDES

**Acyl Halides**,  $\text{R}-\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{X} \end{smallmatrix}$ , may be regarded as acids in which

the OH of the COOH group is replaced by a halogen:



(The acyl chloride compounds are common, but few of the corresponding iodide and bromide compounds are known, and they are used only infrequently.)

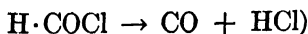
**Nomenclature.**—The group  $\text{R}-\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \end{smallmatrix}$  is known as the “acyl” group.

The group  $\text{CH}_3-\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \end{smallmatrix}$  is known as the “acetyl” group.

The group  $\text{C}_2\text{H}_5-\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \end{smallmatrix}$  is known as the “propionyl” group.

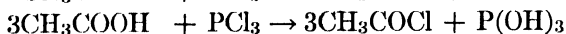
Therefore, in naming the acyl halide, we need merely change the *ic* (last two letters) of the acid to *yl*.

(Formyl chloride is not known. When the attempt is made to prepare it, it breaks down into CO and HCl:



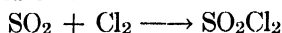
**Acetyl chloride** finds extensive use in organic syntheses and its preparation and properties will, therefore, be considered.

**Preparation.** 1. By the action of phosphorus pentachloride, phosphorus trichloride, or phosphorus oxychloride on acetic acid, or sodium acetate:

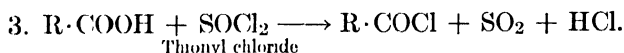


These reactions are analogous to those of  $\text{ROH} \rightarrow \text{RCl}$ . (See p. 43.)

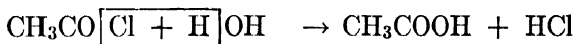
2. The commercial method of obtaining the chloride is to heat sodium acetate and to pass sulfur dioxide and chlorine over it. The sulfur dioxide and chlorine combine to form sulfuryl chloride:



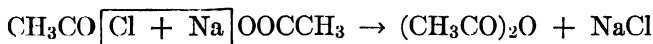
which then reacts with the sodium acetate:



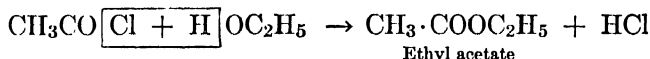
**Properties.**—Acetyl chloride is used extensively to introduce the  $\text{CH}_3\text{—C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \end{smallmatrix}$  (**acetyl**) group into organic compounds. It is a very reactive substance. The moisture of the atmosphere very readily converts it to acetic acid:



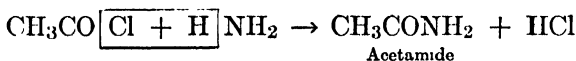
Acetyl chloride reacts with sodium acetate to form acetic anhydride:



and with ethyl alcohol to form an ester:



and with ammonia to form an amide:

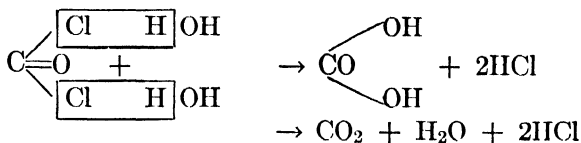


If the OH groups in carbonic acid,  $\text{C} \begin{smallmatrix} \nearrow \text{OH} \\ \searrow \text{OH} \end{smallmatrix}$  are replaced by Cl,

we get  $\text{C} \begin{smallmatrix} \nearrow \text{Cl} \\ \searrow \text{Cl} \end{smallmatrix}$  (chloro-formyl chloride), which is commonly known

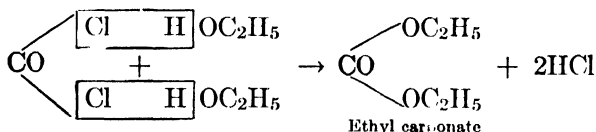
as **phosgene**. This substance is a colorless, suffocating gas. Owing to its poisonous character, the comparative ease with which it can be liquefied and prepared (by passing chlorine and carbon monoxide over charcoal), phosgene was used very extensively in the late war. It was loaded in shells and bombs and exploded when the shell struck ground. Phosgene is also used in the manufacture of dyes.

Water decomposes phosgene as follows:

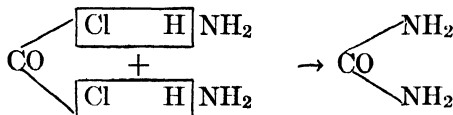


(The poisonous effects of phosgene are said to be due to the liberation of a high concentration of HCl gas.)

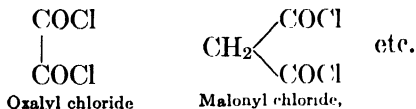
Ethyl alcohol forms an ester:



Ammonia transforms phosgene into urea (or carbamide):



Other acyl halides are:



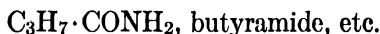
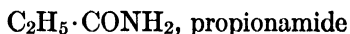
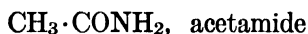
#### ACID AMIDES

**Acid Amides**,  $\text{R}-\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{NH}_2 \end{array}$ , may be looked upon as acids in

which the OH group is replaced by  $\text{NH}_2$ . Or, they may be regarded as derived from ammonia,  $\text{NH}_3$ , in which one of the hydrogen atoms is replaced by the RCO (acyl) group. The

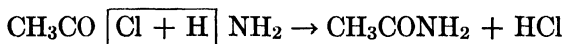
—NH<sub>2</sub> group when attached to an acyl group is known as the “amido” group. If the —NH<sub>2</sub> group is attached to an alkyl group, it is known as the “amino” group.

The nomenclature is based on the names of the corresponding acids (amides of acids); e.g.,

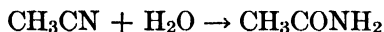


(With the exception of formamide, which is a liquid, all the others are solids.)

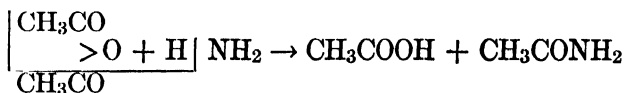
**Preparation and Properties.**—(Acetamide will be taken as a type.) 1. The action of ammonia on acetyl chloride:



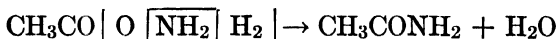
2. The partial hydrolysis of methyl cyanide:



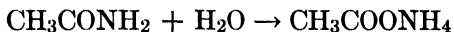
3. The action of ammonia on acetic anhydride:



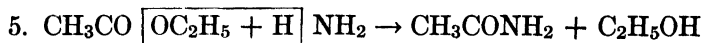
4. The dehydration of ammonium acetate (by heating):



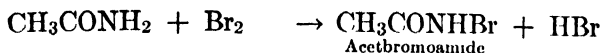
Acetamide is transformed into ammonium acetate when boiled with acids or bases (compare with reaction 4 above):



and when dehydrated forms methyl cyanide (compare with reaction 2 above);



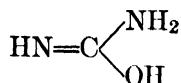
**Hofmann's reaction.**—This is a method by which the CO group can be eliminated from an amide, so that R·CONH<sub>2</sub> becomes RNH<sub>2</sub> (amine). When acetamide is treated with bromine in an alkaline solution the following reactions take place:



**Urea** (carbamide or aminoformamide),  $\text{CO} \begin{array}{l} \nearrow \text{NH}_2 \\ \searrow \text{NH}_2 \end{array}$ , may be

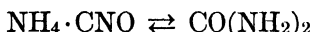
considered as the diamido derivative of carbonic acid,  $\text{CO} \begin{array}{l} \nearrow \text{OH} \\ \searrow \text{OH} \end{array}$ .

Its imide formula is



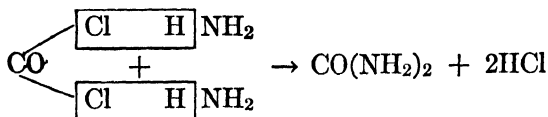
This is a substance of great biological importance, since it is the chief end product resulting from the changes that proteins undergo in the body. (The amount of urea in the urine is directly proportional to the amount of protein present in the food which is eaten.)

**Preparation.**—1. By heating ammonium cyanate:

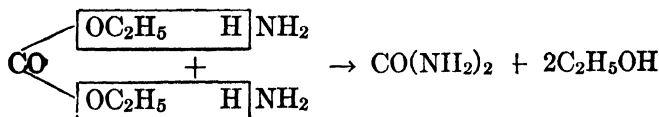


This method was discovered by Wöhler in 1828. The student will recall that Wöhler's preparation is one of the earliest recorded instances of the laboratory preparation of an "organic" substance (p. 1).

2. By the action of ammonia on phosgene:



3. By the action of ammonia on ethyl carbonate:

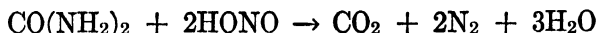


4. A very recent process depends upon the interaction of liquid  $\text{NH}_3$  and liquid  $\text{CO}_2$ :



This synthetic urea is now used extensively as a fertilizer.

**Properties.**—Urea is easily hydrolyzed, yielding carbon dioxide and ammonia. These same products are also obtained when the enzyme urease (found in the soya bean, etc.) is allowed to act on urea. (Incidentally, by far the best method for the determination of urea is based on its reaction with urease.) Nitrous acid liberates nitrogen, etc.:



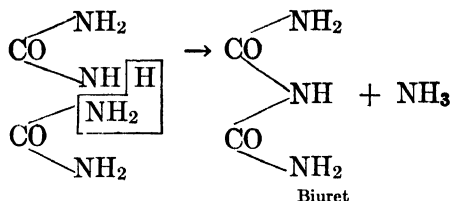
So does sodium hypobromite:



(This method was for a long time used to determine urea. The nitrogen evolved was measured, and from it the amount of urea in the sample was calculated. The determination at best is only approximate for the errors involved are high. The method has been entirely replaced by the urease method.)

Urea combines very readily with nitric and oxalic acids to form urea nitrate,  $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$ , urea oxalate,  $[\text{CO}(\text{NH}_2)_2]_2 \cdot (\text{COOH})_2$ , respectively. These salts crystallize very readily and are often used for identifying urea.

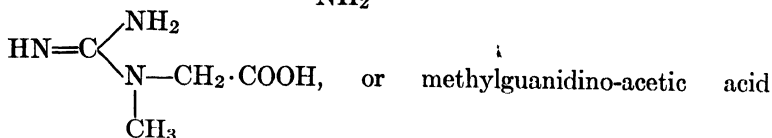
When urea is heated, two molecules combine to form a substance known as **biuret**:



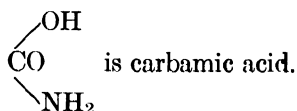
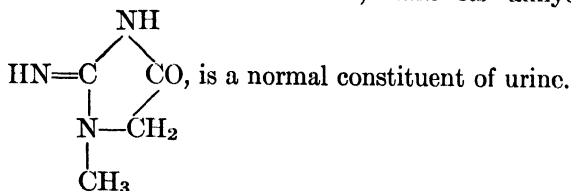
When a drop of copper sulfate and a few cc.'s of fairly concentrated alkali are added to biuret, a violet color is formed. This is known as the "biuret reaction." All proteins give the biuret reaction—a reason for assuming that the protein molecule has, among other things, a "biuret" configuration.

Urea combines with formaldehyde to form synthetic resins.

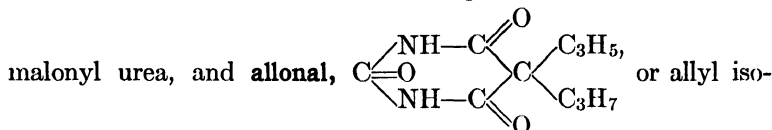
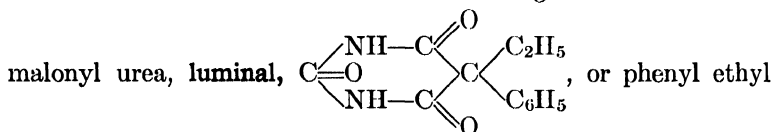
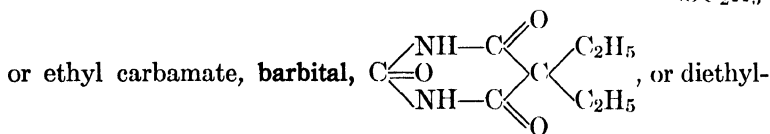
**Guanidine**,  $\text{HN}=\text{C} \begin{matrix} \text{NH}_2 \\ \text{NH}_2 \end{matrix}$ , is related to urea. **Creatine**,



is a constituent of muscle; and its anhydride, **creatinine**,

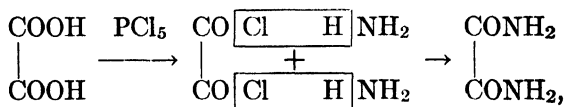


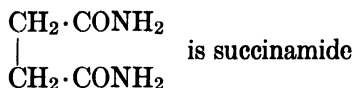
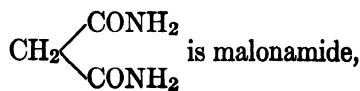
(A number of derivatives of urea, such as urethane,  $\begin{matrix} \text{NH}_2 \\ \diagup \\ \text{C} \\ \diagdown \\ \text{OC}_2\text{H}_5 \end{matrix}$ ,



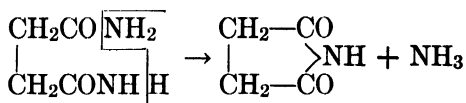
propyl malonyl urea (allyl isopropyl barbituric acid), are used extensively as hypnotics.)

**Oxamide**,  $\begin{matrix} \text{CONH}_2 \\ | \\ \text{CONH}_2 \end{matrix}$ , is formed as follows:





When succinamide is heated, we get succinimide, the  $\text{>NH}$  group being known as the imido group:



#### READING REFERENCES

WERNER—The Chemistry of Urea.

ANON—Barbital (Veronal) and Barbital Compounds. *Journal of the American Medical Association*, **84**, 465 (1925).

DYSON—Phosgene. *Chemical Reviews*, **4**, 109 (1927).

KRASE, GADDY AND CLARK—Direct Synthetic Urea Process. *Industrial and Engineering Chemistry*, **22**, 289 (1930).

SHONLE—Hypnotic Action and Chemical Structure. *Industrial and Engineering Chemistry*, **23**, 1104 (1931).



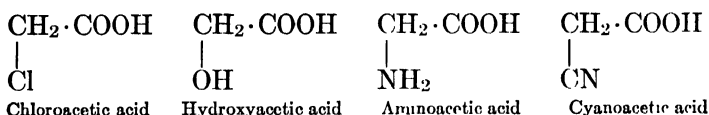
## CHAPTER XII

### HALOGEN SUBSTITUTED ACIDS AND HYDROXY ACIDS

THESE are acids in which one or more of the hydrogen atoms in the group, which is attached to the COOH group, is replaced by X, OH, CN, NH<sub>2</sub>, etc. For example, CH<sub>2</sub>·COOH, acetic acid,

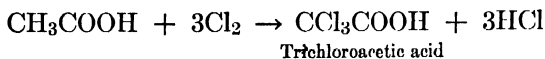
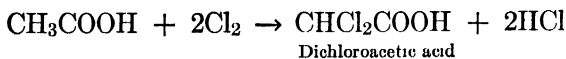
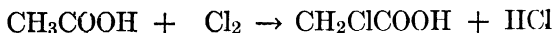


gives rise to



#### HALOGEN SUBSTITUTED ACIDS

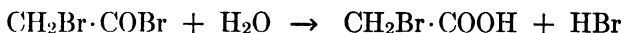
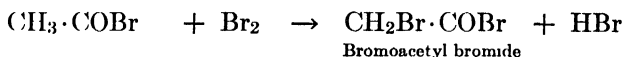
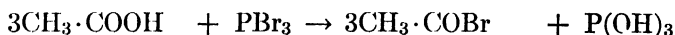
**Preparation.**—The action of chlorine on acetic acid:



(The number of hydrogen atoms replaced by chlorine atoms depends upon the amount of chlorine used, the temperature and the time of the reaction. These reactions are carried out in the presence of sunlight and "carriers"—catalysts—such as iodine or sulfur.)

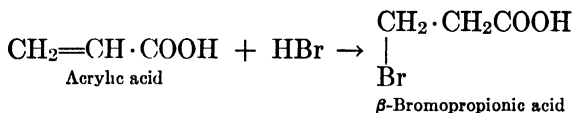
Analogous compounds may be formed by substituting bromine for chlorine, but here the reaction proceeds only under pressure and at higher temperatures. Iodine does not react. (In order to make such a substance as iodoacetic acid, we allow potassium iodide to react with chloroacetic acid: CH<sub>2</sub>Cl·COOH + KI → CH<sub>2</sub>I·COOH + KCl.)

Better yields are obtained in the following way:



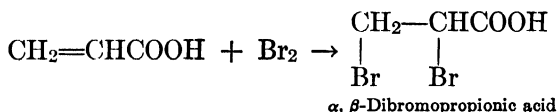
Direct halogenation always replaces the hydrogen attached to the  $\alpha$ -carbon. The nomenclature may be gathered from this graphic illustration:— $\underset{\delta}{\text{CH}_2}$ — $\underset{\gamma}{\text{CH}_2}$ — $\underset{\beta}{\text{CH}_2}$ — $\underset{\alpha}{\text{CH}_2}$ —COOH.

The  $\beta$ -halogenated acids may be obtained in the following way:

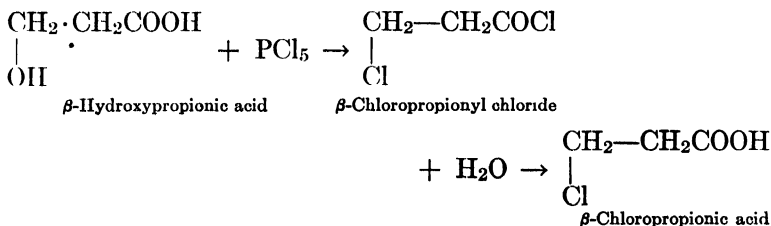


(The halogen enters the position as far removed from the COOH group as possible.)

$\alpha$ - and  $\beta$ -halogenated acids may be prepared thus:

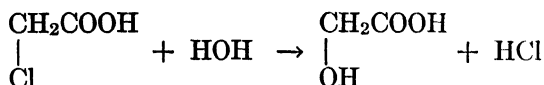


Halogenated acids may also be prepared from hydroxy-acids:

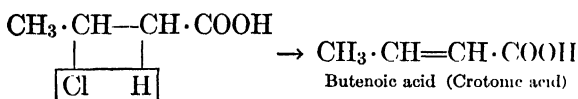


**Properties.**—Some of the properties (such as the formation of salts, esters, etc.) are due to the presence of a carboxyl group and some to the radical attached to the carboxyl group. For example, the greater the number of halogens attached to the carboxyl group, the stronger the acidity. Trichloroacetic acid,

$\text{CCl}_3\text{COOH}$ , is a strong acid. The  $\alpha$ -halogen acids in the presence of hot alkali yield the corresponding hydroxy-acids:

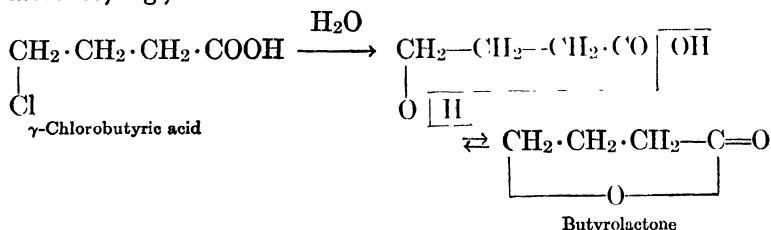


The  $\beta$ -halogen acids yield unsaturated acids when heated with water or alcoholic KOH; e.g.,

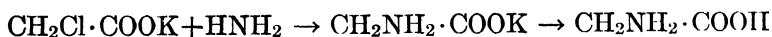


(In certain cases—where, for example, sodium carbonate is used— $\text{CO}_2$  is also evolved, so that butenoic acid is converted to the corresponding unsaturated hydrocarbon,  $\text{CH}_3 \cdot \text{CH} = \text{CH}_2$ .)

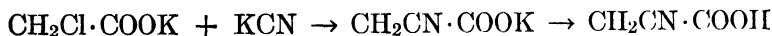
The  $\gamma$ -halogen acids form with water inner anhydrides or lactones; e.g.,



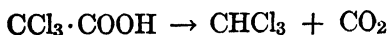
With ammonia, the halogen-substituted acids form amino-acids:



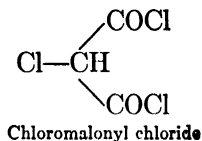
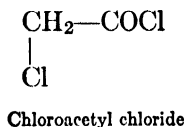
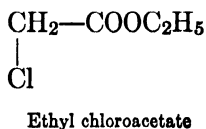
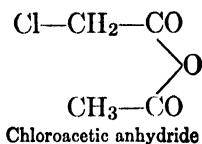
With potassium cyanide, we get the cyano-acids; e.g.,



Very many of these halogen-substituted products are known. Chloroacetic acid,  $\text{CH}_2\text{Cl} \cdot \text{COOH}$ , is used in the manufacture of synthetic indigo. The vapors attack the eyes, and they also act corrosively on the skin. Trichloroacetic acid,  $\text{CCl}_3 \cdot \text{COOH}$ , also acts corrosively on the skin and is used to remove warts and other growths. It has recently come into use as a protein precipitant. When boiled with water we get chloroform:

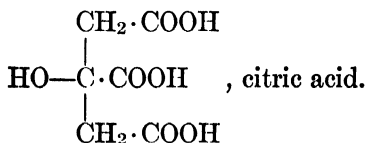
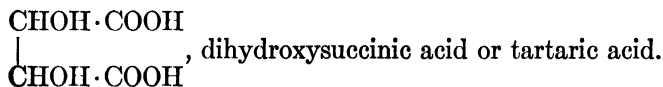
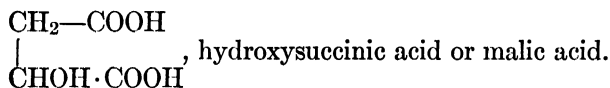
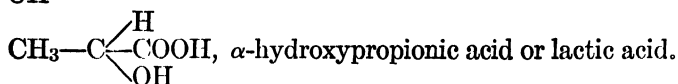
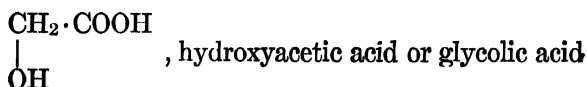
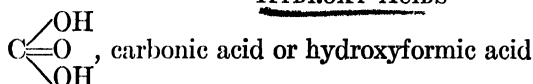


Many other halogenated acids of higher molecular weight are known. It is also possible to have halogenated acid derivatives. For example,

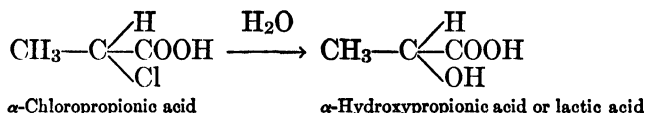


etc.

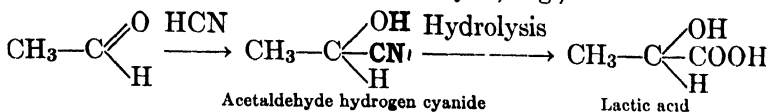
### HYDROXY ACIDS



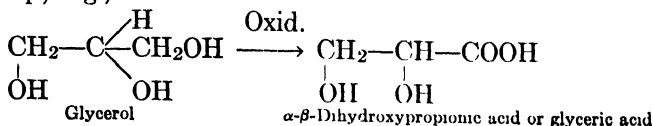
**General Methods of Preparation.**—1. Hydrolysis of halogen acids (base); e.g.,



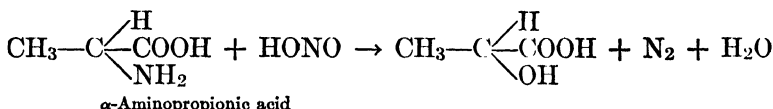
2. The hydrolysis of the addition product formed when hydrogen cyanide reacts with an aldehyde; e.g.,



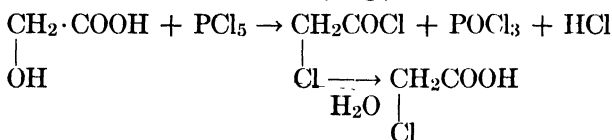
3. The oxidation of a primary alcohol containing another hydroxyl group; e.g.,



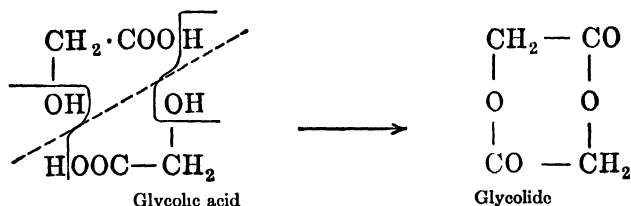
4. Action of nitrous acid on amino-acids; e.g.,



**Properties.**—As might be expected, these compounds show the properties both of hydroxy and carboxylic substances. The chloro-acids are formed with  $\text{PCl}_5$ ; e.g.,



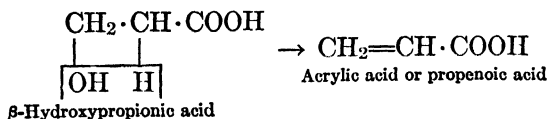
When the  $\alpha$ -hydroxy-acids are heated, two molecules unite with the elimination of two molecules of water:



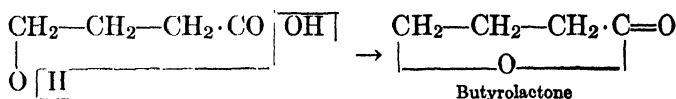
In a similar manner lactic acid is converted to lactide.

When  $\beta$ -hydroxy acids are heated, we get unsaturated acids;

e.g.,



When  $\gamma$ -hydroxyacids are heated an inner anhydride (lactone) is formed; e.g.,



This is also true of  $\delta$ -hydroxyacids.

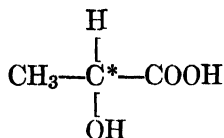
Hydroxyacetic acid,  $\text{CH}_2\text{OH}\cdot\text{COOH}$  (also known as **glycolic acid**) occurs in unripe grapes.

$\alpha$ -Hydroxypropionic acid,  $\text{CH}_3-\text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{COOH} \\ \diagdown \\ \text{OH} \end{array}$  (better known

as **lactic acid**), is known in three forms, the dextro and levo optically active modifications, and the racemic, or inactive form (which can, however, be resolved into the two optically active forms).

**Optical Activity.**—Three forms of lactic acid are known. These three varieties have the same chemical and physical properties but behave quite differently towards polarized light. One turns the plane of polarized light to the right (and is, therefore, known as dextro, or *d*-lactic acid); the other turns it to the left (levo, or *l*-variety); and the third is inactive (*dl*). This last is made up of equal parts of the dextro and levo forms.<sup>1</sup>

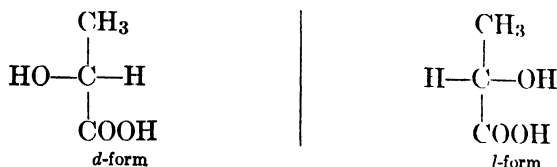
Le Bel and van't Hoff, quite independently of one another, discovered that all optically active substances have at least one carbon in the molecule attached to four different atoms or groups. For example, in lactic acid:



we have a carbon atom marked\* which is attached to H, OH,  $\text{CH}_3$  and  $\text{COOH}$ . Such a carbon atom is known as an **asymmetric carbon atom**.

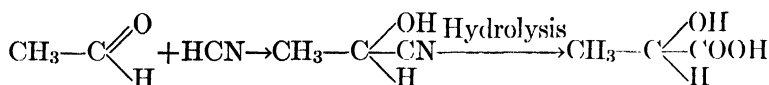
<sup>1</sup> By polarized light we mean light in which all the vibrations lie in one plane. An ordinary ray of light vibrates in every direction. Polarized light may be obtained by passing ordinary light through a Nicol prism or tourmaline plate—as illustrated in the instrument known as the “polarimeter.” An optically active substance has the power of rotating this plane of polarized light, the extent depending, among other things, upon the nature of the substance. For further details, consult a practical physical chemistry; for example, Firth—Practical Physical Chemistry.

Structurally, the *d*-form of lactic acid is related to the *l*-form as an object is to its mirror image:



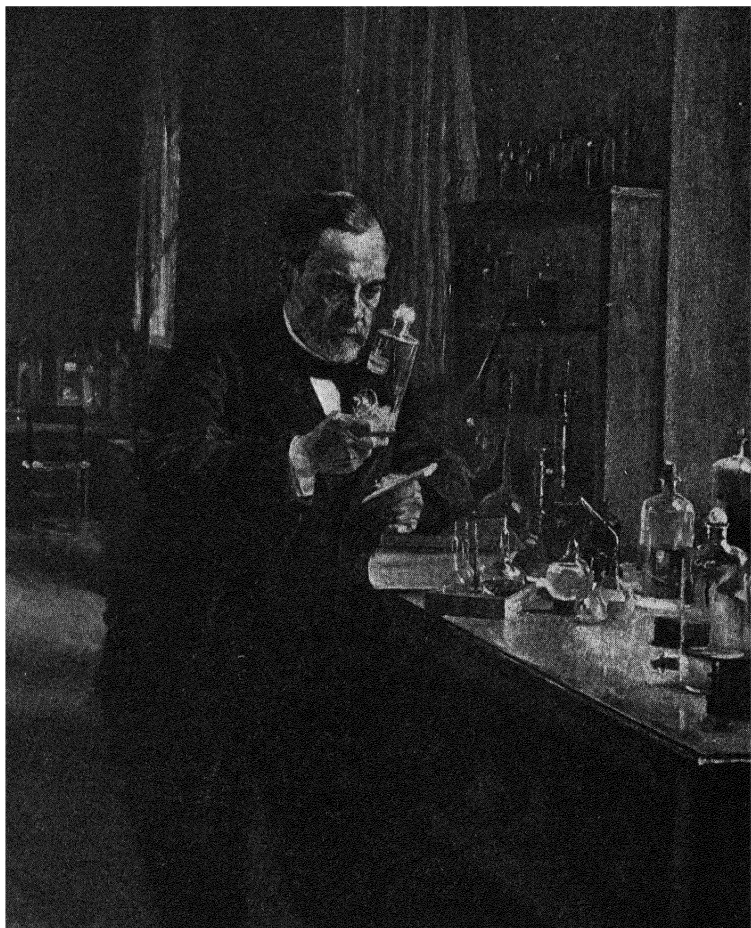
Usually, when a compound containing an asymmetric carbon atom is synthesized, we get equal parts of the dextro and levo varieties. Such a mixture is designated as *dl*-, or *i* (inactive), and is known as "racemic." This inactive mixture can, as a rule, be resolved into the active constituents in a number of different ways. One of these depends upon the property which certain organisms possess of destroying one component more rapidly than another. For example, bacteria destroy the *l*-lactic acid and penicillium the *d*-lactic acid.

The souring of milk is due to the formation of lactic acid (the inactive variety), and this is brought about by the action of certain bacteria (which are also present in the air) on the milk sugar or lactose present in the milk. The acid so formed precipitates the principal protein (caseinogen) in milk, giving rise to what is known as "curdling." The synthetic lactic acid of commerce is prepared from acetaldehyde, as follows:



Lactic acid is manufactured in the United States by the comparatively high temperature fermentation of cane or beet sugar, corn starch or corn sugar, by a pure culture of lactic acid bacteria. It is a colorless, viscous liquid and is used in medicine, dyeing and calico printing. The antimony, zinc and iron lactates are used as mordants. Silver lactate is a powerful antiseptic. Ethyl lactate is one of the best solvents for nitrocellulose and is therefore extensively used in the lacquer industry.

Dextro-lactic acid, or *d*-lactic acid (also called sarcolactic acid and paralactic acid) is found in muscle tissue, meat extract, blood and urine. Inactive muscle is alkaline and after activity it becomes acid, a change which has been ascribed to the formation



### LOUIS PASTEUR (1822-1895)

CHEMIST, FOUNDER OF THE MODERN SCIENCE OF BACTERIOLOGY AND ONE OF THE GREATEST SCIENTISTS OF ALL TIMES. ONE OF HIS EARLIEST RESEARCHES DEALT WITH THE CRYSTALLINE FORMS OF TARTARIC ACID AND ITS SALTS (P. 132), AND THIS LED DIRECTLY TO LE BEL AND VAN'T HOFF'S CONCEPTION OF STEREOISOMERISM.



of lactic acid. When the *d*-acid is heated it loses its optical activity and is converted to the inactive or *dl*-variety.

Levo-lactic acid, or *l*-lactic acid, is obtained when sugar is fermented with *bacillus acidi levolactici*.

The *d*- and *l*- lactic acids and the *dl*- or *i*- variety show the same physical and chemical properties; they differ only as regards optical activity.

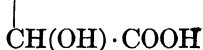
(The intermediate changes that proteins, fats and particularly sugars undergo in the body in their ultimate breakdown to carbon dioxide, water and simple nitrogenous bodies, are associated with the formation, it is believed, of lactic acid, among other substances. The evidence is accumulating to show that lactic acid is an important intermediate product in the decomposition within the body of the common foodstuffs.)

(An isomer of lactic acid is  $\beta$ -hydroxypropionic acid, or hydracrylic acid,  $\text{CH}_2\text{—CH}_2\cdot\text{COOH}$ , in which the hydroxyl

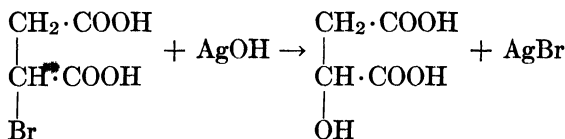


group is in the  $\beta$ -position.)

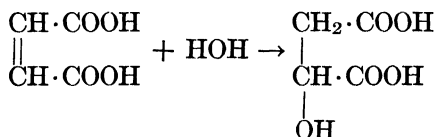
Hydroxysuccinic acid,  $\text{CH}_2\cdot\text{COOH}$  (commonly known as



**malic acid**) is present in unripe apples, cherries, grapes, etc. It may be prepared from bromosuccinic acid by the action of silver hydroxide:

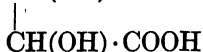


The commercial method of preparation is from maleic acid:



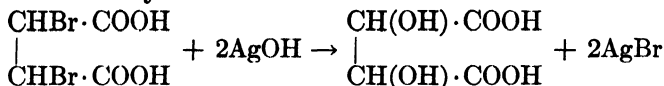
Malic acid is optically active and has the general properties of hydroxy acids.

Dihydroxysuccinic acid,  $\text{CH(OH)}\cdot\text{COOH}$  (commonly known

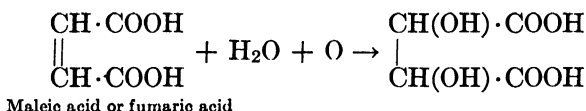


as **tartaric acid**), contains two hydroxyl groups and is a dibasic

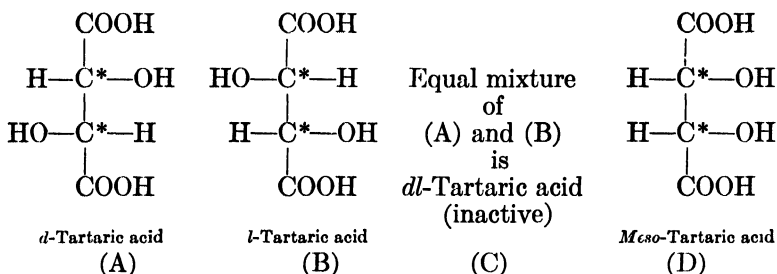
acid. It can be prepared from dibromosuccinic acid by the action of silver hydroxide:



The reduction of tartaric acid (with hydrogen iodide) first yields malic acid and then succinic acid. Interesting, also, is the fact that maleic acid, or fumaric acid, representing the unsaturated dibasic acids, may be converted to tartaric acid by oxidation with potassium permanganate:



The following four forms of tartaric acid are known:



Thus we have two forms of tartaric acid which are optically active [(A) and (B)]; and two which are optically inactive [(C) and (D)]. (A) is the mirror image of (B), while in (D) the upper part of the graphic formula is a mirror image of the lower part. (C) can be resolved into the *d*- and *l*-forms, while (D) cannot. (C) is said to be optically inactive by external compensation, while (D) is optically inactive by internal compensation.

*d*-Tartaric acid is the one found in grapes in the form of potassium acid tartrate. *l*-Tartaric acid may be obtained from the inactive form by "splitting" or resolution into the active isomers.

Racemic (inactive) or *dl*-acid, is found in grapes and is formed when the *d*-acid is boiled with NaOH solution. It may be resolved into the *d*- and *l*-forms.

A fourth variety, *meso*-tartaric acid (first prepared by Pasteur by heating the cinchonine salt of *d*-tartaric acid) is also inactive, but, unlike the racemic acid, cannot be resolved into the *d*- and *l*-forms.

(The history of tartaric acid is intimately associated with the development of our ideas of optical activity and of the asymmetric carbon atom; and with these ideas the names of Pasteur, van't Hoff and Le Bel will forever be linked. It was Pasteur who first showed that the racemic acid was really a mixture of two types of crystals, one the image of the other, and that when mechanically separated and dissolved in water, the one type turned polarized light to the right and the other turned it to the left, suggesting at once that the racemic acid was really a mixture of the *d*- and *l*-forms. The later researches of van't Hoff and Le Bel connected optical activity with the presence of one or more asymmetric carbon atoms within the molecule. There are two asymmetric carbon atoms in the molecule of tartaric acid; these have already been referred to.)

**Salts of Tartaric Acid.** — Potassium acid tartrate,  $\text{CH(OH) \cdot COOK}$  (also known as **cream of tartar**) is a constituent

$$\begin{array}{c} | \\ \text{CH(OH) \cdot COOH} \end{array}$$

of baking powders, and is used in dyeing.

Sodium potassium tartrate,  $\text{CH(OH) \cdot COOK \cdot 4H_2O}$  (commonly known as **Rochelle salt**), is a constituent of Fehling's solution and is also used as a purgative (in "Seidlitz" powders).

$$\begin{array}{c} | \\ \text{CH(OH) \cdot COONa} \end{array}$$

Potassium antimonyl tartrate,  $\text{CH(OH) \cdot COOK}$  (also known

$$\begin{array}{c} | \\ \text{CH(OH) \cdot COO(SbO)} \end{array}$$

as **tartar emetic**), is used in medicine as an emetic, and also in dyeing.

**Citric acid**,  $\text{CH}_2 \cdot \text{COOH}$ , is a monohydroxy tribasic acid, and

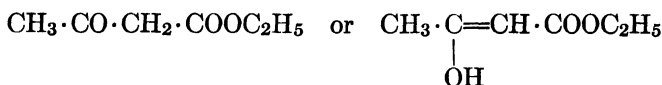
$$\begin{array}{c} | \\ \text{HO—C—COOH \cdot H}_2\text{O} \\ | \\ \text{CH}_2 \cdot \text{COOH} \end{array}$$

is found in lemons (from the juice of which it is commonly prepared), berries, limes and other acidulous fruits. It is also prepared on large scale by the fermentation of glucose or sucrose, by certain mould fungi as *citromycetes pfefferianus*. It is used in lemonade and other beverages, and in calico printing.

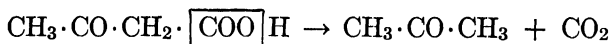
**Magnesium citrate**  $(\text{C}_6\text{H}_5\text{O}_7)_2\text{Mg}_3$  is used as a laxative, and

ferric ammonium citrate, in blue-print paper manufacture and in calico printing. Sodium citrate is used extensively for the prevention of blood coagulation.

**Acetoacetic acid**,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COOH}$ , or acetyl acetic acid, and its ethyl ester, acetoacetic ester,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$  are here considered because the ester may be looked upon as a derivative of a  $\beta$ -hydroxy unsaturated acid:

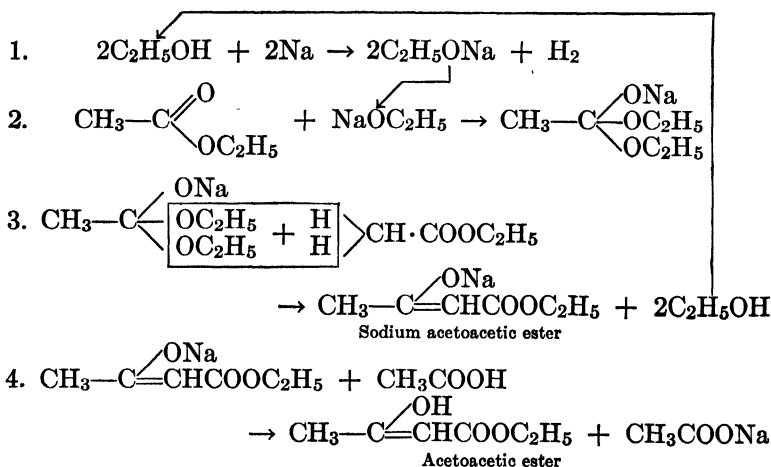


Acetoacetic acid is one of the "acetone bodies" present in the urine of persons suffering from diabetes, and it is commonly known as "diacetic acid." It is an unstable acid and decomposes into acetone:

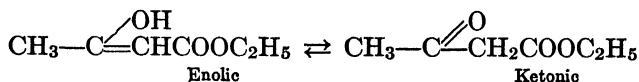


which explains the presence of acetone in the urine and breath of diabetics.

Acetoacetic ester,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$  (or, more correctly, ethyl acetoacetate) is a compound of considerable importance in synthetic organic chemistry. Claisen's explanation of its synthesis, which follows, is the one generally accepted to-day:



Tautomeric forms:

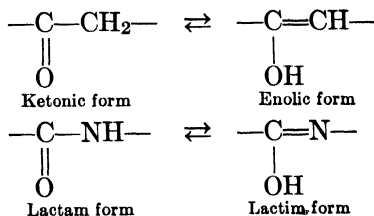


Acetoacetic ester is prepared by the action of sodium on ethyl acetate. A small amount of alcohol is needed for reaction (1); additional quantities of alcohol are formed as shown in (3).

The enolic form  $\left(-\overset{\text{OH}}{\underset{\text{C}}{\text{=}}}\text{CH}-\right)$ , first produced [see (4)], rearranges to the more stable keto form  $\left(-\overset{\text{O}}{\underset{\text{C}}{\text{=}}}\text{CH}_2-\right)$ . An equilibrium mixture of the enolic and ketonic forms contains 7 per cent and 93 per cent respectively.

(The type of isomerism wherein, under certain conditions, a compound passes from one structural form into another, is known as **tautomerism**.)

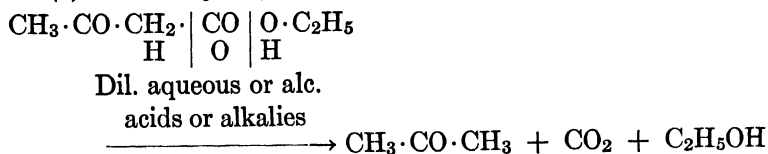
This is characteristic of many compounds having the carbonyl group attached to a carbon or nitrogen atom to which also one or more hydrogens are attached.



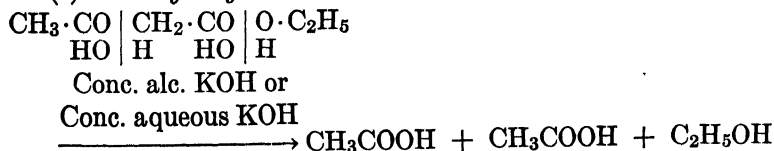
Acetoacetic ester is a colorless liquid with a fruity odor.

**Uses of Acetoacetic Ester.**—Depending upon the reagents used, as well as the concentration of solutions, the following two types of decomposition take place:

(a) *Ketonic hydrolysis*:



(b) *Acid hydrolysis*:

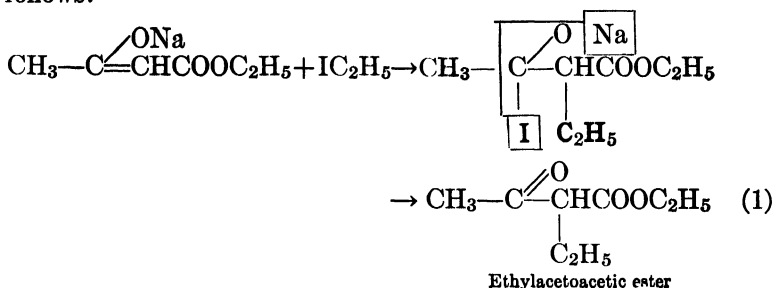


One or both hydrogens in the  $-\text{CO} \cdot \text{CH}_2-$  part of the acetoacetic ester may be replaced by various groups, giving rise to substituted acetoacetic ester derivatives. (A somewhat analogous

case may be found in malonic ester, p. 103.) If one mole of sodium ethylate reacts with one mole of acetoacetic ester, the compound

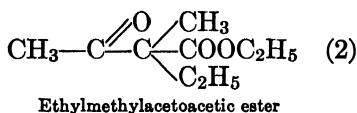


is produced. This reacts with an alkyl halide, for example, as follows:

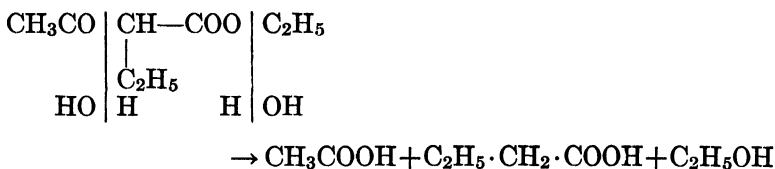


(1) still contains a replaceable hydrogen atom  $\left( -\text{C} \begin{array}{l} \text{O} \\ || \\ \text{CH}- \\ \searrow \text{C}_2\text{H}_5 \end{array} \right)$

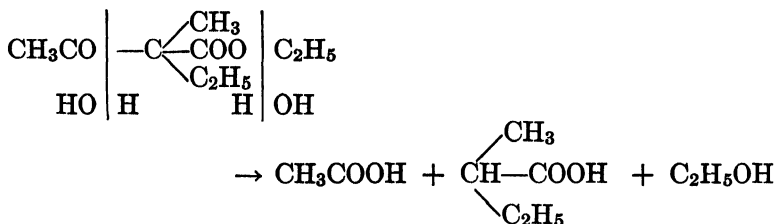
and by means of a series of analogous reactions another alkyl group may be introduced, giving, for example:



On *acid hydrolysis*, (1) decomposes thus:

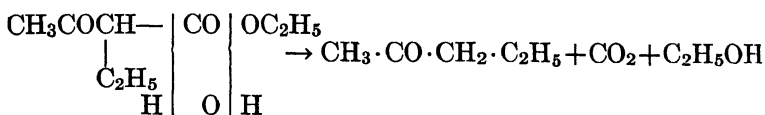


and (2):

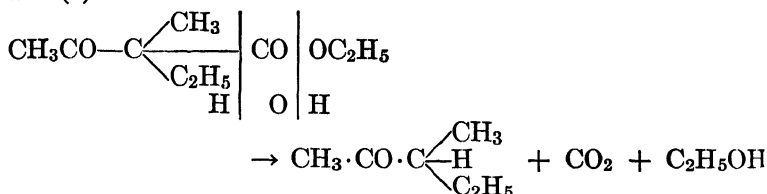


which means that we are able to build up (synthesize) mono-  
basic acids of the types  $R-CH_2COOH$  and  $\begin{matrix} R \\ R \end{matrix} > CHCOOH$ .

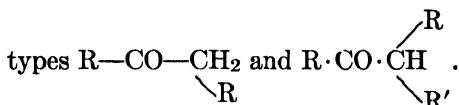
On *ketonic hydrolysis*, (1) decomposes thus



and (2):



which means that we are able to synthesize higher ketones of the



Acetoacetic ester is also used in the manufacture of anti-  
pyrine—p. 306—and a number of dyes.)

# READING REFERENCES

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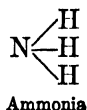
GARRETT—Lactic Acid. *Industrial and Engineering Chemistry*, **22**, 1153 (1930).

MAY AND HERRICK—Citric Acid. *Industrial and Engineering Chemistry*, **22**, 1172 (1930).

## CHAPTER XIII

### AMINES OR ORGANIC BASES

THESE compounds are derivatives of ammonia:



Ammonia



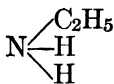
Primary  
amine



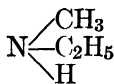
Secondary  
amine



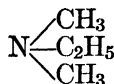
Tertiary  
amine



Ethylamine



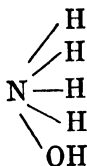
Ethyl methyl-  
amine



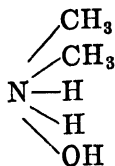
Dimethyl  
ethylamine

(In  $\text{R} \cdot \text{NH}_2$  the  $-\text{NH}_2$  is an amino group, in  $\begin{array}{c} \text{R} \\ \diagup \\ \text{N} \\ \diagdown \\ \text{R} \end{array} \text{NH}$  the  $=\text{NH}$  is an imino group).

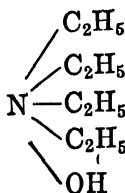
We have similar relationships in  $\text{NH}_4\text{OH}$ , where one or more hydrogens in the  $\text{NH}_4$  group may be replaced by R groups.



Ammonium hydroxide

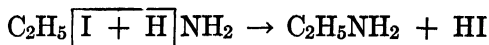


Dimethylammonium hydroxide



Tetraethylammonium hydroxide

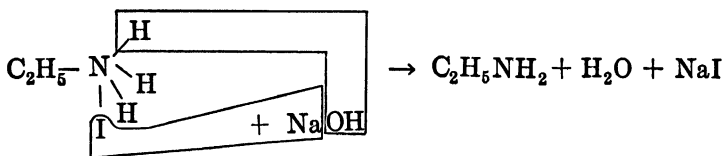
**Methods of Preparation of Primary Amines.**—1. Theoretically the simplest method should involve the reaction between ammonia and an alkyl halide:



but due to the basicity of  $\text{C}_2\text{H}_5 \cdot \text{NH}_2$ , an addition compound ( $\text{C}_2\text{H}_5\text{NH}_3\text{I}$ , ethylammonium iodide) is first formed, which may

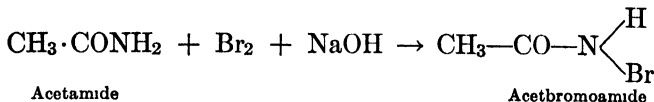


be decomposed by means of alkali just as an ammonium salt may be decomposed by means of alkali:



(This method is little used because of complicated secondary reactions which take place (p. 140) ).

2. The action of bromine and a strong base on an amide, e.g.,

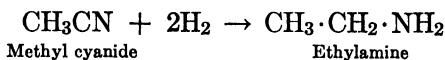


In brief,  $\text{CH}_3 \cdot \text{CONH}_2 \rightarrow \text{CH}_3 \cdot \text{NH}_2$

(This is known as the *Hofmann* reaction.)

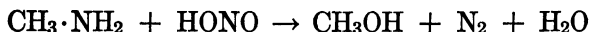
Notice that the conversion of acetamide to methylamine involves the loss of a carbon atom. The *Hofmann* reaction is often used in the conversion of one member of a series to another containing one less carbon atom. (See indigo, p. 309.)

3. The reduction of alkyl cyanides; e.g.,



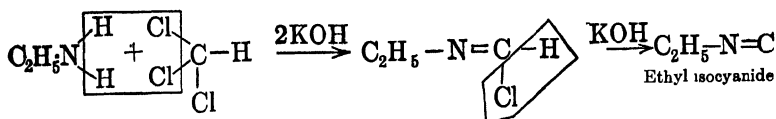
**Properties of Primary Amines.**—These compounds are more basic than ammonia and are readily soluble in water. They have a strong, fish-like odor, and their vapors are flammable. They combine with acids, giving such compounds as methylammonium bromide,  $\text{CH}_3\text{NH}_2 \cdot \text{HBr}$ ; methylammonium nitrate,  $\text{CH}_3\text{NH}_2 \cdot \text{HNO}_3$ , and methylammonium sulfate  $(\text{CH}_3\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$ .

The amines are acted upon by nitrous acid, yielding the corresponding hydroxy compounds:



(The *Van Slyke* method for determining the rate of hydrolysis of a protein is based on this reaction. See under amino acids, p. 146.)

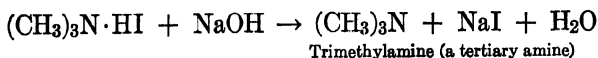
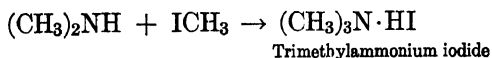
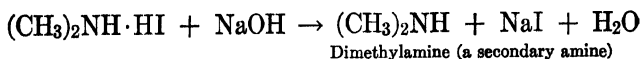
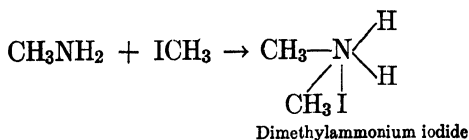
✓ Chloroform and alcoholic potassium hydroxide react with primary amines with the formation of isocyanides (isonitriles).



(This is known as the **carbylamine reaction** and is used to distinguish primary from secondary and tertiary amines. The isocyanides have characteristic and highly disagreeable odors.)

Methylamine is a common constituent of many putrefactive mixtures.

**Secondary and tertiary amines** may be obtained by the following series of reactions:

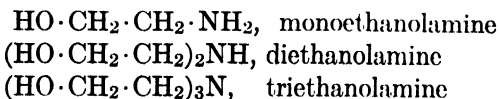


(Trimethylamine can combine with methyl iodide to form tetramethylammonium iodide  $(\text{CH}_3)_4\text{N} \cdot \text{I}$ . Since the reactions given above proceed more or less simultaneously, it becomes somewhat difficult to separate the different amines.)

(For another method see p. 240.)

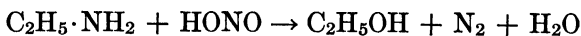
The physical properties of the secondary and tertiary amines are similar to those of the primary amines. Dimethylamine is used in the manufacture of rubber accelerators. Trimethylamine is produced by the destructive distillation of the residue obtained in the sugar beet industry. They, and the primary compound, are found in herring brine and in the products obtained from the distillation of nitrogenous substances.

By the action of ammonia on ethylene oxide we get the following:

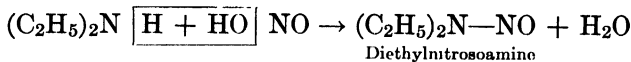


These compounds are viscous, hygroscopic liquids. They are organic bases of mild alkalinity and react with fatty acids to produce soaps which are used in dry cleaning. These soaps are excellent emulsifying agents. Triethanolamine is a very good absorbent for acid gases.

**The Action of Nitrous Acid on Primary, Secondary and Tertiary Amines.**—It has already been stated that the action of nitrous acid on a primary amine forms the corresponding hydroxy compound: e.g.,



With secondary amines, nitrous acid forms nitroso compounds e.g.,

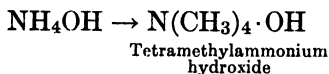


(The nitroso-compounds are usually yellow-colored, volatile liquids of aromatic odor.)

Tertiary compounds do not react with nitrous acid (though oxidation of an indefinite type may take place).

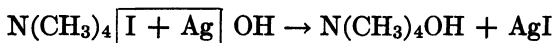
Nitrous acid is, therefore, used to distinguish the amines. (The "carbylamine reaction" given above, p. 140, is specific for primary amines.)

"Quaternary bases" are compounds related to ammonium hydroxide; e.g.,



(Choline, neurine and muscarine, compounds of physiological importance—See Chapter X—may be regarded as derivatives of quaternary bases.)

Tetramethylammonium hydroxide may be prepared thus:

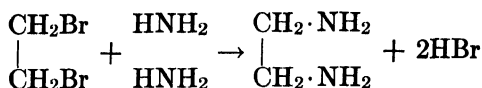


It is a colorless, hygroscopic solid, the solution of which is strongly basic, resembling potassium hydroxide. When heated, it decomposes into trimethylamine:



which is really a very good method for the preparation of tertiary amines.

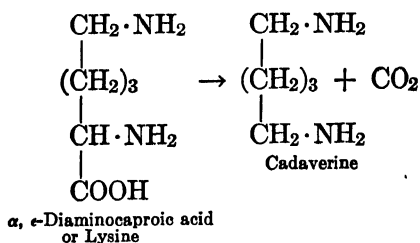
Compounds containing two amino groups are known as diamines: Ethylenediamine may be made from ethylene bromide:



Trimethylene diamine has the formula  $\text{CH}_2 \begin{array}{l} \nearrow \text{CH}_2\cdot\text{NH}_2 \\ \searrow \text{CH}_2\cdot\text{NH}_2 \end{array}$

Tetramethylene diamine,  $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2 \\ | \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2 \end{array}$  or **putrescine**, and

pentamethylenediamine,  $(\text{CH}_2)_5(\text{NH}_2)_2$ , or **cadaverine**, are putrefactive products of the corresponding amino acids, ornithine and lysine (p. 148), and are found among the putrefactive products in the intestine. It is the belief that the putrefactive products in the intestine are formed by the action of bacteria on various amino acids, which are converted into the corresponding amines by loss of  $\text{CO}_2$ ; e.g.,



(The chemical properties of the diamines are similar to the monoamines, except that as we have to consider two primary  $\text{NH}_2$  groups instead of one  $\text{NH}_2$  group.)

(For a group of compounds related to the amines and of great physiological importance, such as choline, neurine, lecithin, betaine and muscarine, see Chapter X, p. 110.)

#### READING REFERENCES

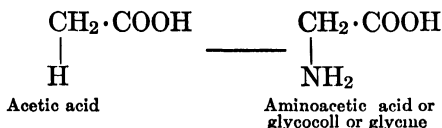
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## CHAPTER XIV

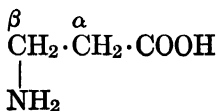
### AMINO ACIDS AND PROTEINS

#### AMINO ACIDS

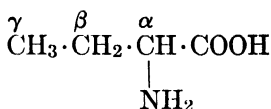
AN amino acid is a compound in which a hydrogen in the group attached to the COOH is replaced by an NH<sub>2</sub> group; e.g.,



(The nomenclature is analogous to that used in the halogen and hydroxy substituted acids, so that



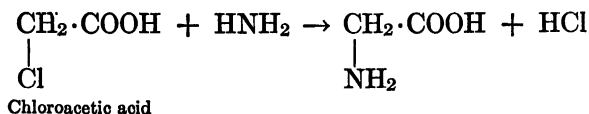
is  $\beta$ -aminopropionic acid; and



is  $\alpha$ -aminobutyric acid.)

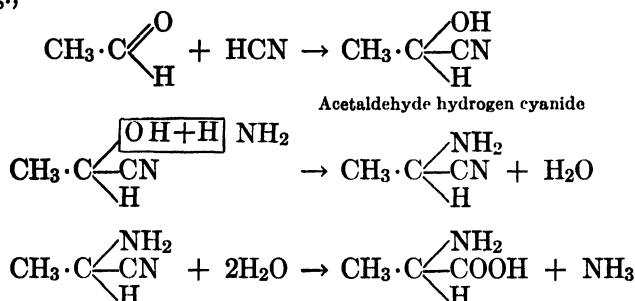
The  $\alpha$ -amino acids are of great importance physiologically, since these are the main products obtained when proteins are hydrolyzed.

**Methods of Preparation.**—1. The action of ammonia on halogen acids; e.g.,



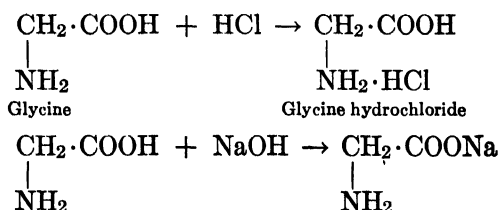
2. The action of hydrogen cyanide on aldehydes and ketones,

and the subsequent reaction with ammonia and ultimate hydrolysis; e.g.,

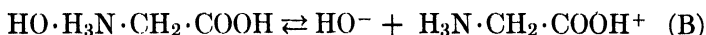
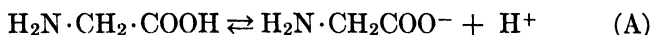


3. The hydrolysis of proteins (either by enzymes, acids or alkalies) yields a succession of products (metaproteins, proteoses, peptones, polypeptides), the final products being amino acids. (In the digestive tract, the enzymes pepsin, trypsin and erepsin hydrolyze the various proteins of the food into different amino acids.)

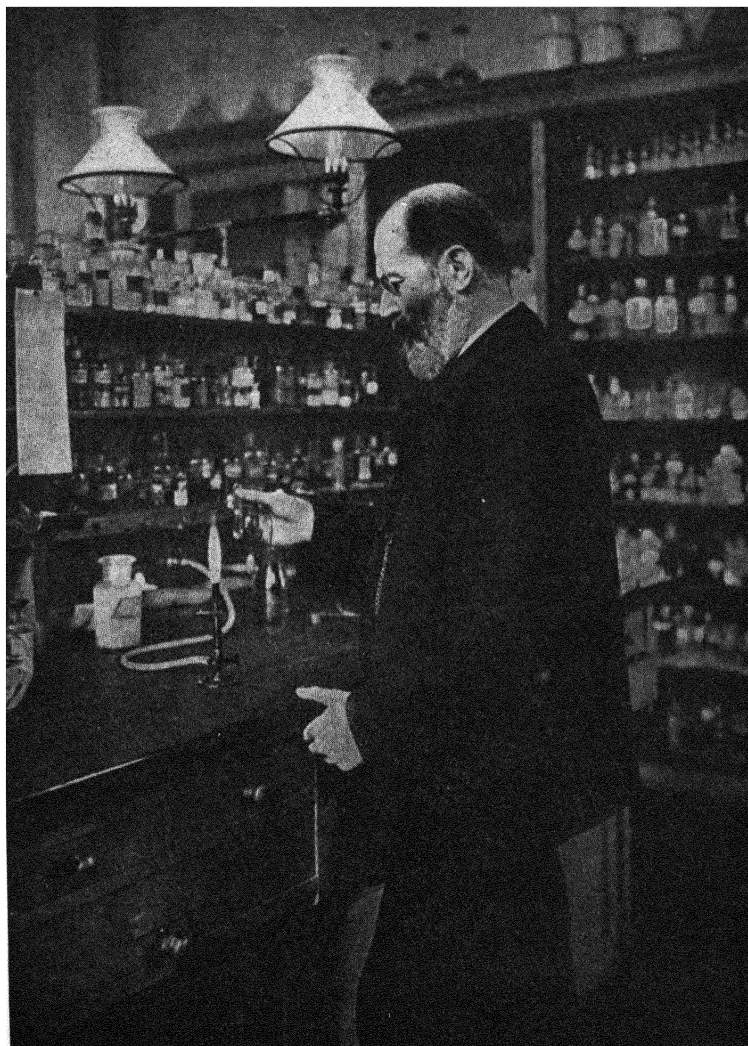
**Properties.**—Since the amino acids contain  $\text{NH}_2$  and  $\text{COOH}$  groups, they may act as bases or acids; e.g.,



(They are, in reality, amphoteric substances, like aluminium hydroxide or zinc hydroxide. Glycine, for example, is a feeble electrolyte and is partially dissociated thus:



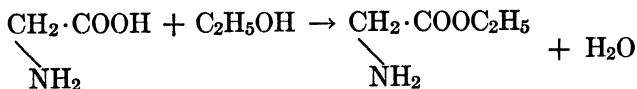
At some particular hydrogen ion concentration, the dissociation represented by (A) will be equal to the dissociation represented by (B). This is the "isoelectric point," and at this point the solution is electrically neutral. The significance of the "isoelectric point" and its bearing on the behavior of such substances as proteins is only now beginning to be appreciated.)



EMIL FISCHER (1852-1919)

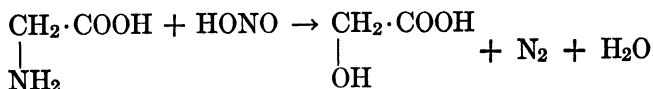
ONE OF THE FOREMOST ORGANIC CHEMISTS OF THE NINETEENTH CENTURY, DID MUCH TO ELUCIDATE THE CHEMISTRY OF CARBOHYDRATES (p. 169), PURINES (p. 155) AND PROTEINS (p. 149).

When dissolved in alcohol and saturated with hydrogen chloride (dehydrating agent), the amino acids form esters; e.g.,



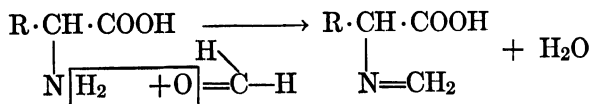
(Emil Fischer has used this "ester" method to separate the amino acids obtained by the hydrolysis of proteins.)

Nitrous acid converts amino acids into the corresponding hydroxy compounds with the liberation of nitrogen; e.g.,



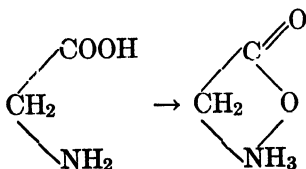
(This is the principle of the *Van Slyke* method for the determination of amino acids in blood and tissues, and for following the rate of protein hydrolysis.)

Aldehydes react with amino acids to form methylene derivatives; e.g.,



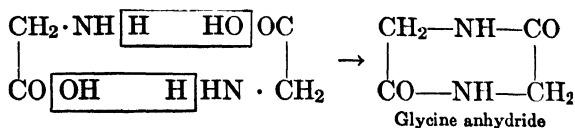
(This reaction converts an approximately neutral substance—because of the presence of the  $\text{NH}_2$  and  $\text{COOH}$  groups—into an acid substance, by a substitution in the  $\text{NH}_2$  group. Sørensen has used this principle for determining amino acids in blood, urine and tissues, and for estimating the extent of protein hydrolysis. The greater the hydrolysis, the more free  $\text{NH}_2$  and  $\text{COOH}$  groups are formed and hence, when the  $\text{NH}_2$  group is removed by formaldehyde, the greater the acidity of the hydrolytic products.)

Since an amino acid contains a basic and an acidic group, internal neutralization is possible, with the resulting formation of "inner" salts:

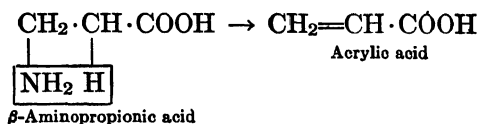




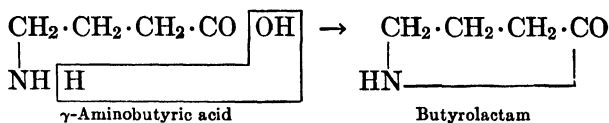
When an  $\alpha$ -amino acid is heated, two of its molecules combine to form an anhydride:



$\beta$ -Amino acids, when heated, lose ammonia and yield unsaturated acids:



$\gamma$ -Amino acids give "lactams":



(These reactions are analogous to those given under hydroxy acids, p. 127.)

Several amino acids obtained from the hydrolysis of proteins are listed.

**Glycocoll**,  $\text{CH}_2 \cdot \text{COOH}$ , also called glycine, is aminoacetic acid.



**Alanine**,  $\text{CH}_3 \cdot \text{CH} \cdot \text{COOH}$ , is  $\alpha$ -aminopropionic acid.



**Valine**,  $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH} \cdot \text{CH} \cdot \text{COOH} \\ \diagup \\ \text{CH}_3 \end{array}$ , is  $\alpha$ -aminoisovaleric acid.



**Leucine**,  $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \\ \diagup \\ \text{CH}_3 \end{array}$ , is  $\alpha$ -aminoisocaproic acid.



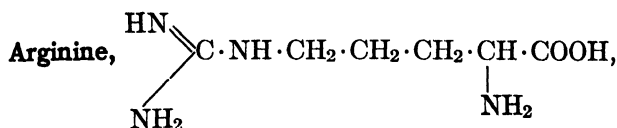
acid.

**Phenyl alanine**,  $\text{CH}_2 \cdot \text{CH} \cdot \text{COOH}$ , is  $\beta$ -phenyl- $\alpha$ -aminopro-

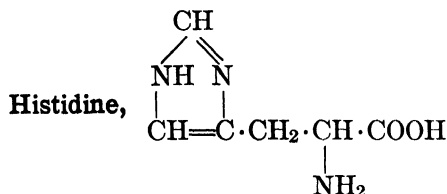


pionic acid.





is  $\alpha$ -amino- $\delta$ -guanidino-valeric acid.



is  $\alpha$ -amino- $\beta$ -imidazolepropionic acid

# PROTEINS

Proteins are essential, and in many ways, the most characteristic constituents of protoplasm. They may be regarded as combinations of  $\alpha$ -amino acids. Their chemical properties are dependent upon the presence of these amino acids. Their physical properties, on the other hand, are largely due to the fact that they form colloidal solutions. Among the three classes of foodstuffs, fats, carbohydrates and proteins, the proteins alone contain the element nitrogen, and, as a rule, sulfur. The average percentage composition of proteins is (in per cent)  $C = 53$ ,  $O = 23$ ,  $N = 16$ ,  $H = 7$ , and  $S = 1$ .

They may be classified as follows:

**Albumins.**—Soluble in water and coagulated on boiling. (Examples: ovalbumin in egg white, lactalbumin in milk, serum albumin in blood, etc.)

**Globulins.**—Insoluble in water, but soluble in dilute solutions of a number of salts (such as sodium chloride) and coagulable on heating. (Examples: serum globulin in blood, edestin in hempseed, ovoglobulin in egg white, etc.)

**Protamines.**—Basic substances forming stable salts with mineral acids. In comparison with some of the other proteins, these yield relatively few amino acids on hydrolysis. They are soluble in water and not coagulated on heating. (Examples: salmine in salmon sperm, and in general, in the heads of ripe spermatozoa and in ova.)

**Histones.**—Somewhat similar to protamines. These are soluble in water and precipitated by ammonia. (Examples: globin in hemoglobin, scombrone in mackerel sperm, thymus histone, etc.)

**Glutelins.**—Proteins common in the vegetable kingdom. These are insoluble in neutral solvents, but soluble in dilute acids and alkalies. (Example: glutenin in wheat.)

**Prolamines.**—These are also common in the vegetable kingdom. They are soluble in 70–80 per cent alcohol (which distinguishes them from glutelins and other proteins), but, like other proteins, insoluble in absolute alcohol. They are also insoluble in water and neutral solvents. (Examples: zein in corn, gliadin in wheat and rye, hordein in barley, etc.)

**Albuminoids.**—These are found in the skeletal and connective tissue of animals, and are characterized by their far greater insolubility in reagents than other proteins. (Examples: keratin in hair, collagen in connective tissue, etc.)

The proteins which have so far been enumerated are known as “simple proteins,” to distinguish them from the following “conjugated proteins”:

**Nucleoproteins.**—These are combinations of protein and nucleic acid, and are characterized by yielding purine bases (p. 151) on hydrolysis. (Examples: nucleoprotein in thymus, pancreas, spleen, and in glandular tissue in general. They are found in nearly all cells, and particularly in the nuclei of cells.)

**Glycoproteins.**—Combinations of protein and a compound containing the carbohydrate group. They are characterized by yielding, on hydrolysis, a sugar which reduces *Fehling's-Benedict* solution. (Examples: mucin in saliva, osseomucoid in bone, tendomucoid in tendon, etc.)

**Phosphoproteins.**—These proteins, like the nucleoproteins, are rich in phosphorus, but, unlike the latter, do not yield purine bases on hydrolysis. (Examples: casein in milk, vitellin in egg yolk, etc.)

**Hemoglobins.**—Combinations of protein with a pigment-containing substance. (Example: hemoglobin in blood, which on hydrolysis yields the histone, globin, and the iron-containing substance, hematin.)

In addition to these, we have a number of “secondary” or “hydrolyzed” proteins, obtained in the course of hydrolysis

of proteins when acted upon by certain enzymes, acids or alkalies. They are:

**Metaproteins.**—These represent the first stage in protein hydrolysis. They are soluble in acids and alkalies, but insoluble in neutral solvents (from which they are coagulated on boiling).

**Proteoses.**—The primary proteoses are soluble in water, not coagulated on boiling, and precipitated by one-half saturated solution of ammonium sulfate. The secondary proteoses show similar properties, except that they require a completely saturated solution of ammonium sulfate for precipitation, a crude distinction, it must be confessed.

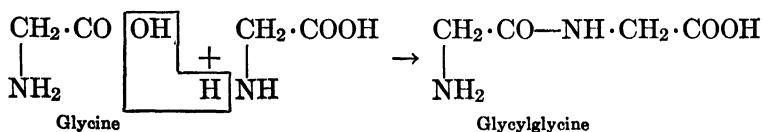
**Peptones.**—These are similar to the proteoses, but are not precipitated by ammonium sulfate.

As hydrolysis proceeds, we arrive at the **polypeptide** stage (compounds of a somewhat simpler type, chemically, than peptones), and finally obtain the individual **amino acids**.

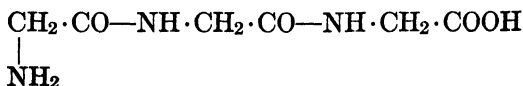
**Composition of Proteins.**—The various proteins, when completely hydrolyzed (by acid, alkali or enzyme) yield amino acids. The essential difference among proteins is in the number and in the amount of amino acids which they yield. Up to the present, about 20 of these amino acids have been isolated (see amino acids, p. 152), and the extent to which they occur in a number of proteins is given in the table on the following page.

The isolation of the various amino acids is a laborious task and cannot be discussed here.

**Constitution of Proteins.**—Emil Fischer has shown that the proteins may be regarded as combinations of amino acids, linked in the following way (to take the simplest case):



Glycylglycine (dipeptide) is the simplest example of a polypeptide. It, in turn, may combine with another molecule of glycine to form diglycylglycine (tripeptide).



PER CENT OF AMINO ACIDS ISOLATED FROM VARIOUS PROTEINS

	Gliadin— Wheat	Salmon— Salmon	Keratin— Sheep's Horn	Ovalbumin— Cryst.	Muscle— Scallop	Japanese— Silk Cocoons	Globin—Horse Hemoglobin	Gelatin	Casein—Cow	Elastin
Glycocoll.....	0.02	0.00	0.45	0.00	0.00	35.00	0.00	16.5	0.45	25.75
Alanine.....	2.00	0.00	1.6	2.22	....	22.6	4.2	0.8	1.85	6.58
Valine.....	0.21	4.3	4.5	2.50	....	....	....	1.0	7.95	1.4
Leucine.....	5.61	0.00	15.3	10.71	8.78	0.7	29.0	2.1	9.7	21.38
Proline.....	7.06	11.0	3.7	3.56	2.28	0.7	2.3	5.2	7.63	1.74
Phenylalanine.	2.35	0.0	1.9	5.07	4.90	1.3	4.2	0.4	3.88	3.89
Aspartic acid..	0.58	0.0	2.5	2.20	3.47	1.3	4.4	0.56	1.77	
Glutamic acid.	42.98	0.0	17.2	9.10	14.88	0.07	1.7	1.88	21.77	0.76
Serine.....	0.13	7.8	1.1	?	....	....	0.6	0.4	0.5	
Cystine.....	0.45	0.0	7.5	?	....	....	0.3	0.0	0.07	?
Tyrosine.....	1.20	0.0	3.6	1.77	1.95	9.7	1.3	0.00	4.5	
Arginine.....	3.16	87.4	2.7	4.91	7.38	...	5.4	7.62	3.81	0.3
Histidine.....	0.61	0.0	?	1.71	2.02	....	11.0	0.4	2.5	
Lysine.....	0.00	0.0	0.2	3.76	5.77	....	4.3	2.75	7.62	
Ammonia.....	5.1	....	?	1.34	1.08	....	..	..	1.61	
Tryptophan...	Pres.	0.0	..	..	Pres.	....	Pres	0.0	1.5	

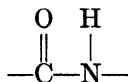
and so on. Of course, the combinations need not involve glycine only, but other amino acids may take a part in such reactions—in fact, any substance containing the  $\text{NH}_2$  and  $\text{COOH}$  groups; so that the number of such possible polypeptides is very large.

Fischer has prepared an octadecapeptide, consisting of three leucine and fifteen glycine units, which is not easily distinguishable from a protein found in nature. Apart from being a colloid, this octadecapeptide is hydrolyzed by the enzyme trypsin (of the pancreas) into amino acids, just like any of the common proteins.

As further evidence of the polypeptide nature of proteins, it should be recalled that when proteins are hydrolyzed, polypeptides (such as glycytyrosine) have actually been isolated from among the hydrolytic products.

**General Reactions.**—*Biuret.*—When the protein is mixed with a conc. solution of sodium hydroxide and a drop or two of dilute copper sulfate solution is added, a violet to pink color is obtained. (Generally the simpler the protein the more pinkish

the color, so that peptones show a distinct pink and albumins a distinct bluish-violet.) The reaction is given by nearly all substances containing two



groups attached to one another, to the same nitrogen atom, or to the same carbon atom. The name "biuret" is derived from the fact that biuret (which is obtained by heating urea, p. 120) gives this reaction.

*Xanthoproteic.*—Heating a protein solution with conc. nitric acid produces a yellow color. This is changed to orange on the addition of an excess of ammonium hydroxide. (The yellow color is dependent upon the formation of a nitro compound.)

*Millon's.*—Heating with Millon's reagent (essentially, mercury dissolved in nitric acid), a brick-red color or precipitate is obtained. (This reaction is given by phenol and phenolic derivatives.) The substance in the protein molecule responsible for this test is probably tyrosine.

*Glyoxylic acid (Hopkins-Cole).*—When the protein is mixed with glyoxylic acid and conc. sulfuric acid added, a violet ring is obtained. (This reaction is due to the presence of tryptophan in the protein molecule.)

*Molisch.*—With alpha-naphthol and conc. sulfuric, the protein solution forms a violet ring. (The reaction is due to the presence of the carbohydrate glucosamine in the protein molecule.)

(While no one of these color tests is evidence of the presence of a protein, any substance which gives two or more of these tests may be suspected of being a protein.) The following reactions are further confirmatory tests.

Proteins are precipitated by the salts of heavy metals, such as lead acetate, mercuric chloride, copper sulfate, etc.

The proteins are precipitated by the "alkaloidal reagents," such as phosphotungstic, phosphomolybdic, tannic, picric acids, etc.

Proteins are precipitated by strong alcohol.

Many of the proteins, like the albumins and the globulins, are coagulated on heating.

Recently proteins from beef blood have been introduced as food products. Serum albumin is mixed with dried egg yolks and used in preparing cakes, cookies, omelets, etc.

An even more important industrial development in the use of proteins is in the production of *karolith*, a product made from the casein of skim milk by hardening it with formaldehyde. The material is really a synthetic horn with advantages over horn itself. Karolith softens when moderate heat is applied and can therefore be bent and embossed. It can be dyed or stained and is now used quite extensively in the manufacture of a variety of buttons, pens, pencils, cigarette holders, etc.

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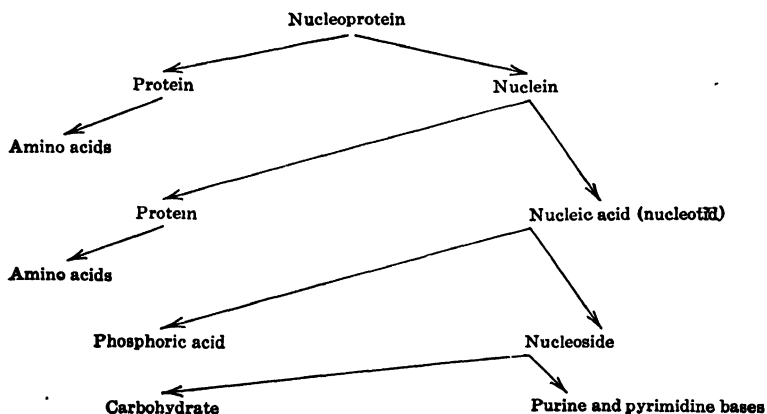


## CHAPTER XV

### NUCLEOPROTEINS, PURINES, URIC ACID AND PYRIMIDINES

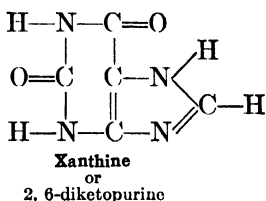
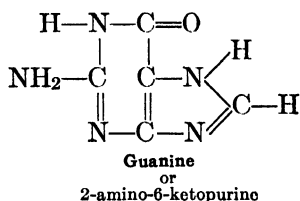
**Nucleoproteins** are a group of combined proteins of especial interest to us, since, on the one hand, they are principally constituents of the nuclei of cells (animal and plant), and on the other, they yield, on decomposition, a group of important organic substances (purines and pyrimidines). They may be extracted from animal or vegetable sources by water or dilute alkali, and precipitated by acid (for example, the nucleoprotein in yeast may be extracted with dilute alkali and then precipitated by acid, or the lymphatic glands of the ox or sheep, or the thymus of a calf, may be extracted with water, and the nucleoprotein precipitated with acid.)

A careful study of the hydrolytic products of nucleoproteins shows that they, like the proteins and higher carbohydrates, "split up" in stages. The following is a schematic representation:

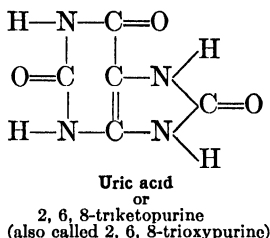


The nucleoprotein, in other words, may be regarded as a combination of protein and nucleic acid, the latter, in turn,



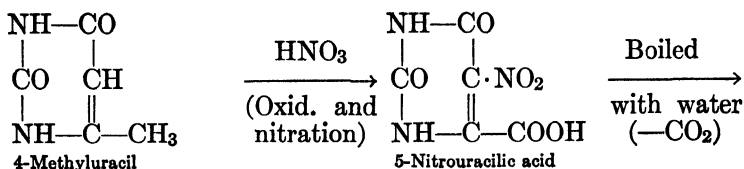
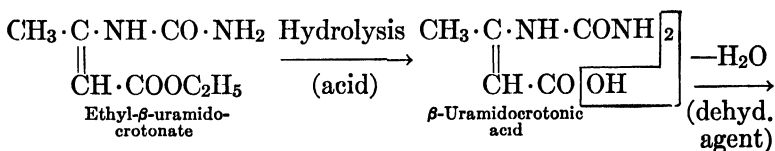
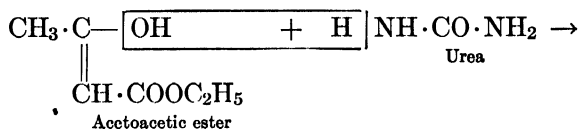


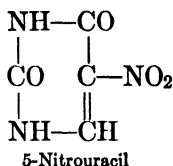
The purines are very largely oxidized to uric acid in the body:



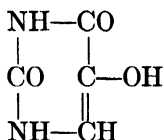
**Uric acid** is an important nitrogenous constituent of the urine. It is present in the joints, bladder, and in abnormally high amounts in the blood of persons suffering from gout and rheumatism.

We shall give one of several syntheses of uric acid. This will illustrate not only the synthetic preparation of an important purine derivative, but incidentally that of a pyrimidine derivative, namely, a methyluracil:

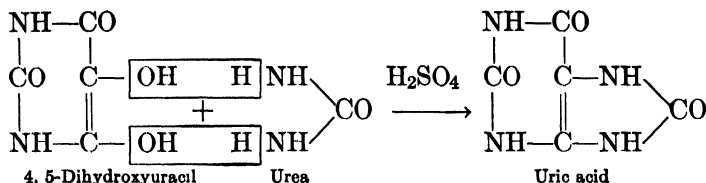




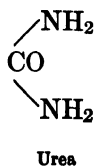
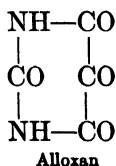
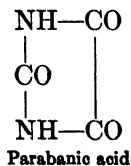
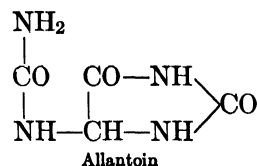
With tin and HCl, part of the 5-nitrouracil is reduced to the corresponding 5-amino-compound (5-aminouracil) and part of it to 5-hydroxyuracil:



This compound is oxidized by bromine water to 4,5-dihydroxyuracil, which, when heated with urea and  $\text{H}_2\text{SO}_4$ , yields uric acid:

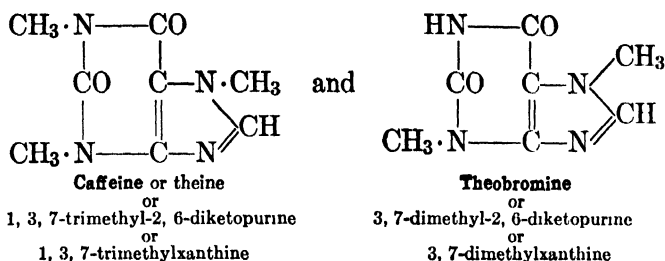


The oxidation of uric acid may yield any one of the following products (depending on the reaction and the reagent employed):



**Allantoin** occurs to a small extent in human urine, but in mammals, other than man and anthropoid apes, it takes the place of uric acid, it being the principal end product of purine metabolism.

Other important purine derivatives are:



Theobromine is present in cocoa beans (chocolate) and **theophylline** (isomeric with theobromine) occurs in tea leaves, while caffeine is a constituent of coffee (about 1 per cent) and tea (about 1-4 per cent).

Caffeine, theobromine and theophylline are strong diuretics, but caffeine is peculiar in having a strong excitant action upon the central nervous system.

## READING REFERENCE

LEVENE AND BASS—Nucleic Acids.

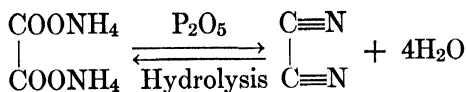
## CHAPTER XVI

### CYANIDES, ISOCYANIDES AND OTHER NITROGEN COMPOUNDS

THE student having taken inorganic chemistry is already familiar, to some extent, with cyanide compounds. He has used potassium ferrocyanide and potassium ferricyanide in testing for iron salts; and he remembers potassium cyanide and hydrogen cyanide as examples of deadly poisons.

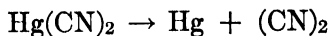
**Cyanogen**  $(\text{CN})_2$ , is a colorless, poisonous gas, with a pungent odor, and burns with a blue flame, giving carbon dioxide and nitrogen. It may be prepared:

1. By heating ammonium oxalate with a dehydrating agent:

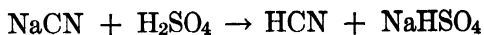


(The cyanogen can be hydrolyzed back to the ammonium oxalate.)

2. By heating mercuric cyanide:

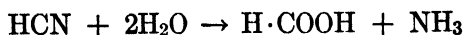


**Hydrogen Cyanide**,  $\text{HCN}$  (also called **hydrocyanic acid**), is a colorless, poisonous volatile liquid, burning with a violet flame. Its water solution is called "prussic acid." (Some attempt was made during the war to use it as a "poison gas.") It occurs in bitter almonds, wild cherry bark and other plant products. It is a very weak acid. Its formula may be represented as  $\text{H}-\text{C}\equiv\text{N} \rightleftharpoons \text{H}-\text{N}=\text{C}$ . It may be prepared by heating sodium cyanide with sulfuric acid:

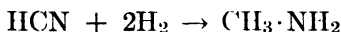


a reaction quite analogous to the preparation of the halogen acids.

Hydrogen cyanide hydrolyzes to formic acid:



and reduces to methylamine:



It is used in medicine (a 2 per cent solution) in respiratory diseases and to quiet a cough. Recently, it has been recommended as a fungicide and insecticide (spraying trees). Ships are very often disinfected with HCN gas.

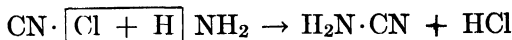
By the action of liquid hydrocyanic acid on calcium carbide (in the presence of a small quantity of water as a catalyst), calcium cyanide,  $\text{Ca}(\text{CN})_2$ , a solid, is obtained. This substance liberates HCN on mere exposure to the air, and, being a solid, can be more easily handled than HCN.

**Cyanogen Chloride**,  $\text{CN} \cdot \text{Cl}$ , is a poisonous liquid of low boiling point, and was used as a "poison gas" in the late war. It may be prepared by the action of chlorine on hydrogen cyanide:

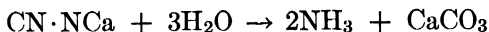


Recently it has been recommended to replace HCN for disinfecting purposes.

**Cyanamide**,  $\text{CN} \cdot \text{NH}_2$ , is prepared by the action of ammonia on cyanogen chloride:



(**Calcium cyanamide**,  $\text{CN} \cdot \text{NCa}$ , made by heating calcium carbide and nitrogen,  $\text{CaC}_2 + \text{N}_2 \rightarrow \text{CaCN}_2 + \text{C}$ , finds extensive use as a fertilizer, for in the presence of water it decomposes in the soil, liberating ammonia:

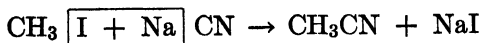


The calcium cyanamide of commerce ( $\text{CaCN}_2 + \text{C}$ ), goes under the name of "nitrolime.")

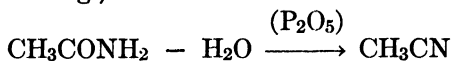
#### ALKYL CYANIDES, $\text{R}-\text{C} \equiv \text{N}$

**Nomenclature.**— $\text{CH}_3\text{CN}$  may be called either methyl cyanide, or cyanomethane, or acetonitrile. The  $-\text{C} \equiv \text{N}$  is the "nitrile" group, and the name of the substance depends upon the acid obtained when the substance is hydrolyzed. For example,  $\text{CH}_3\text{CN}$  is acetonitrile because it hydrolyzes to acetic acid. Similarly,  $\text{C}_2\text{H}_5 \cdot \text{CN}$  is propionitrile.

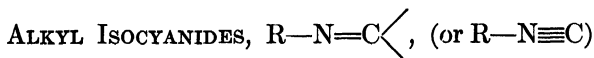
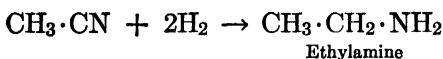
**Preparation.**—1. The action of  $\text{NaCN}$  on an alkyl halide; e.g.,



2. Heating the corresponding amide in the presence of a dehydrating agent: e.g.,



**Properties.**—The alkyl cyanides are reactive on account of their unsaturated character (a triple linkage):

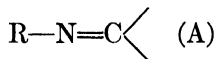


**Nomenclature.**  $\text{CH}_3\cdot\text{N}=\text{C} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$  may be called methyl isocyanide or methyl carbylamine. ( $\text{C}_2\text{H}_5\text{—N}=\text{C} <$  is commonly spoken of as “carbylamine.”)

In organic cyanides the R is connected to the carbon atom:

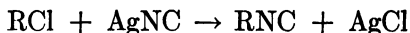


whereas in the organic isocyanides the R is connected to nitrogen:



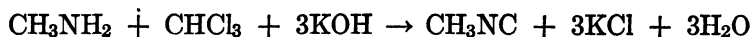
[The formula (A) is selected because the isocyanides are highly reactive substances, forming, among other things, additive compounds.]

**Preparation.**—1. Action of silver cyanide on alkyl halide; e.g.,



(which suggests that silver cyanide may exist in one of two forms, either as  $\text{AgCN}$  or  $\text{AgNC}$ ).

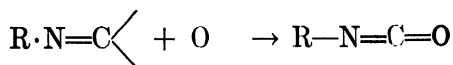
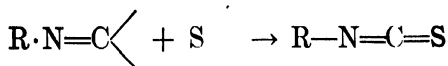
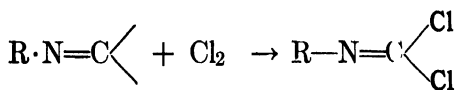
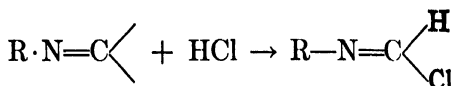
2. The reaction of a primary amine with chloroform in an alkaline solution; e.g.,



(This is a test for primary amines. See p. 140.)

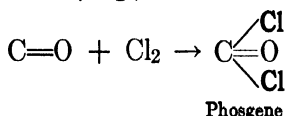
**Properties.**—The isocyanides are colorless, poisonous liquids, with an extremely disagreeable and characteristic odor. They are very reactive; e.g.,





(The C in  $\text{R} \cdot \text{N}=\text{C} \begin{array}{l} \diagup \\ \diagdown \end{array}$  seems to be very reactive and, therefore, unsaturated.)

(In this connection, it may be of interest to point out here that the reactivity of carbon monoxide is in reality due to the divalency of its carbon atom, e.g.,

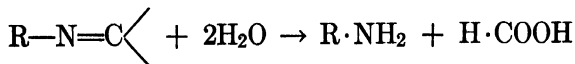
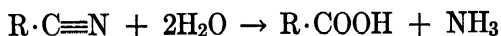


or



whereby the divalent carbon is transformed into the tetravalent form.)

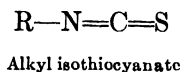
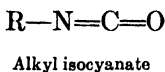
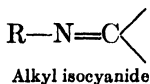
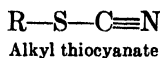
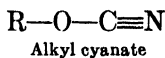
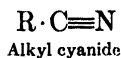
To distinguish between the cyanide and the isocyanide, it is merely necessary to hydrolyze the compounds:



We may also distinguish them by reduction:

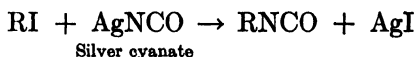


## OTHER NITROGEN COMPOUNDS

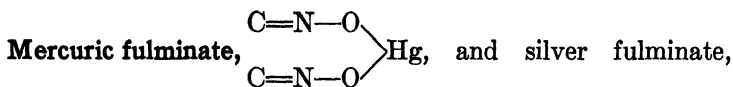


Isocyanic acid,  $\text{HNCO}$ , is an unstable liquid, but a polymer, cyanuric acid  $(\text{HNCO})_3$  is known.

$\text{RNCO}$  compounds are prepared thus:

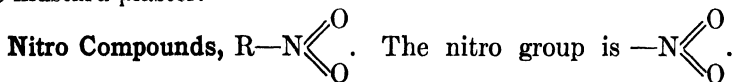


**Fulminic Acid**,  $\text{C}=\text{NOH}$ , is a poisonous, very unstable liquid. Here again we have a divalent carbon represented.



$\text{C}=\text{N}-\text{OAg}$ , are prepared when the respective metals are acted upon by nitric acid and alcohol. They are used as detonators in percussion caps to explode gunpowder, dynamite, T.N.T., and other explosives.

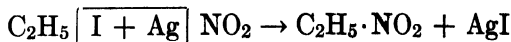
**Allyl isothiocyanate**,  $\text{CH}_2=\text{CH} \cdot \text{CH}_2 \cdot \text{N}=\text{C}=\text{S}$ , is present in black mustard seeds and is used in medicine as a powerful rubefacient and counterirritant. It is employed as a substitute for the mustard plaster.



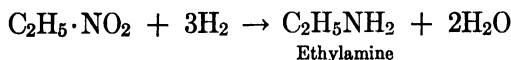
These may be looked upon as nitric acid,  $\text{HO}-\text{N} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$ , in which the OH is replaced by R. The aliphatic nitro compounds are not important, but the aromatic ones are, as we shall see later (p. 230). The nitro compounds,  $\text{R}-\text{N} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$ , are isomeric with the alkyl nitrites,  $\text{R}-\text{O}-\text{N}=\text{O}$ , which have already been discussed on p. 100. For example, nitroethane,  $\text{C}_2\text{H}_5-\text{N} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$  is

isomeric with ethyl nitrite,  $\text{C}_2\text{H}_5\text{—O—N=O}$ , though it differs from ethyl nitrate,  $\text{C}_2\text{H}_5\text{—O—N}\begin{smallmatrix} \text{O} \\ \text{//} \\ \text{O} \end{smallmatrix}$ .

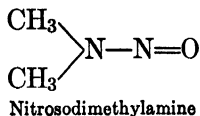
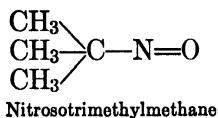
The nitro compounds may be prepared by the action of silver nitrite on halogen compounds; e.g.,



They are easily reduced to the corresponding amines; e.g.,



The nitroso group is represented by  $\text{—N=O}$ ; e.g.,



## READING REFERENCES

- GROTTA—Development and Application of Initiating Explosives. *Industrial and Engineering Chemistry*, **17**, 134 (1925).  
 METZGER—Calcium Cyanide. *Industrial and Engineering Chemistry*, **18**, 161 (1926).  
 SIDGWICK—Structure of Divalent Carbon Compounds. *Chemical Reviews*, **9**, 77 (1931).

## CHAPTER XVII

### CARBOHYDRATES <sup>1</sup> AND RELATED COMPOUNDS

THE name **carbohydrate** (carbon hydrate) is derived from the fact that compounds belonging to this class contain C, H and O, the H and O being in the proportion of 2 : 1, respectively (as in water). There are, however, substances other than carbohydrates, such as acetic acid, ( $\text{CH}_3 \cdot \text{COOH}$ ), and lactic acid ( $\text{CH}_3 \cdot \text{CHOH} \cdot \text{COOH}$ ), which contain H and O in the proportions such as are found in water. On the other hand, a number of compounds belong to the carbohydrates although the proportion of H to O is not 2 : 1; e.g., rhamnose ( $\text{C}_6\text{H}_{12}\text{O}_5$ ).

The more modern view is to regard carbohydrates as containing aldehyde-alcohol or ketone-alcohol groups; or compounds which upon hydrolysis are converted into substances containing such groups. (Organic Type Formulas, p. 16.)

Carbohydrates are mainly derived from the vegetable kingdom. Physiologically, the carbohydrates represent one of the three great classes of foodstuffs. Many of them are also of extreme importance in the industries.

In general, carbohydrates fall into two main classes; the sweet and crystalline compounds, called sugars; and the tasteless and non-crystalline compounds, termed starches, celluloses and allied products.

Carbohydrates are classified into:

*A. Monosaccharides* (no further hydrolysis with dilute acids):

Diose,  $\text{C}_2\text{H}_4\text{O}_2$ , as glycolaldehyde,  $\text{CH}_2\text{OH} \cdot \text{CHO}$ .

Trioses,  $\text{C}_3\text{H}_6\text{O}_3$ , as glyceraldehyde,  $\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{CHO}$   
or dihydroxyacetone,  $\text{CH}_2\text{OH} \cdot \text{CO} \cdot \text{CH}_2\text{OH}$ .

Tetroses,  $\text{C}_4\text{H}_8\text{O}_4$ , as erythrose, etc.

Pentoses,  $\text{C}_5\text{H}_{10}\text{O}_5$ , as arabinose, xylose, ribose, etc.

Hexoses,  $\text{C}_6\text{H}_{12}\text{O}_6$ , as glucose, mannose, galactose, fructose, sorbose, etc.

*B. Disaccharides*,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  (yield two molecules of monosaccharides upon hydrolysis). Sucrose, maltose, lactose.

<sup>1</sup> Recently The International Union of Pure and Applied Chemistry proposed the term "**Glucides**" for carbohydrates and glucosides.

C. *Trisaccharides*,  $C_{18}H_{32}O_{16}$  (yield upon hydrolysis three molecules of monosaccharides):

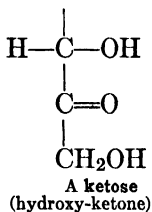
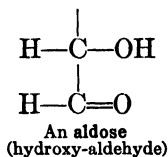
Raffinose.

D. *Polysaccharides*,  $(C_6H_{10}O_5)_x$ , (yield upon hydrolysis more than three molecules of monosaccharides):

Starch, cellulose, dextrin, glycogen, inulin, gums, pectins, pentosans, etc.

(The ending "ose" generally refers to carbohydrates.)

The **monosaccharides**, or simple sugars, are aldehydes or ketones linked directly to carbon with OH group as

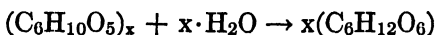


The trioses and tetroses are of theoretical rather than practical importance.

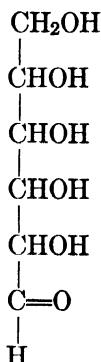
The **pentoses** in the form of more complex combinations, the *pentosans*, occur extensively in the plant kingdom and are found more particularly in the pectins and gummy substances of plants. The pentoses are obtained from the pentosans by hydrolysis with acids. Treated with concentrated hydrochloric acid and distilled, furfural is obtained (see p. 304), a process which forms the basis for the estimation of pentoses and pentosans. Among the more common pentose sugars are **arabinose**, obtained by hydrolyzing gum arabic; **xylose**, obtained by the hydrolysis of straw; and **ribose**, a constituent of nucleic acid (p. 155), found in yeast.

Extremely important, from our point of view, are the hexoses, the disaccharides and some of the polysaccharides.

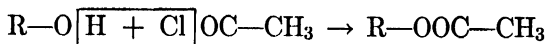
Among the **hexoses**,  $C_6H_{12}O_6$ , *d*-**glucose** (also called dextrose) is the most important. It is present in the juice of many sweet fruits, such as grapes (hence grape-sugar). It is a normal, and very necessary constituent of blood, and, in pathological conditions (as in diabetes), accumulates to an abnormal degree in the blood and in the urine. Commercially, glucose is prepared by the hydrolysis of starch in presence of dilute acids.



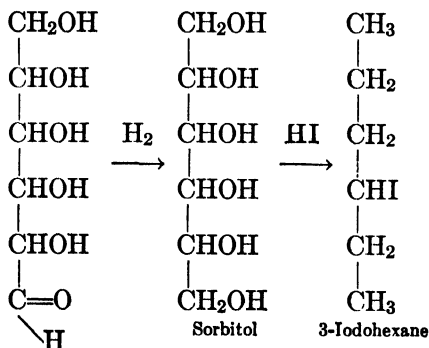
It may be obtained from many poly- and disaccharides. Since it rotates the plane of polarized light to the right, it is also called dextrose or *d*-glucose. Its formula may be written:



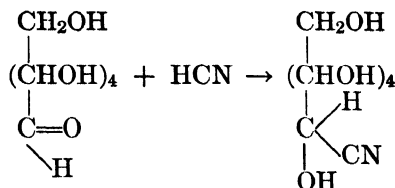
Some indication of how we arrive at such a structural formula may be given. In the first place, elementary analysis and molecular weight determinations give us the empirical formula  $\text{C}_6\text{H}_{12}\text{O}_6$ . The substance behaves like an alcohol, because it reacts with acetyl chloride or acetic anhydride to form acetyl derivatives:



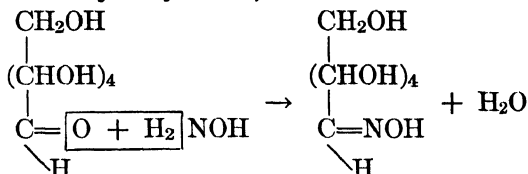
Since glucose forms a penta-acetyl derivative, it must contain five OH groups. On reduction, glucose first yields the corresponding alcohol, and ultimately (if HI is used) a normal six-carbon chain iodohydrocarbon, proving glucose to contain a normal chain of carbon atoms:



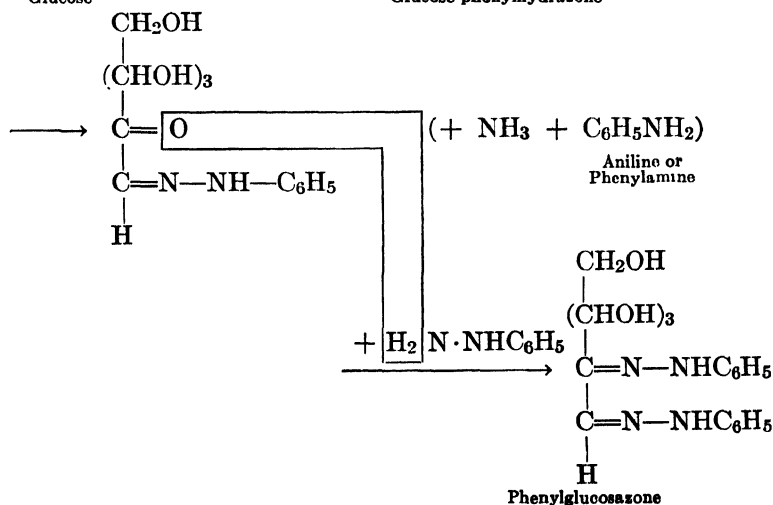
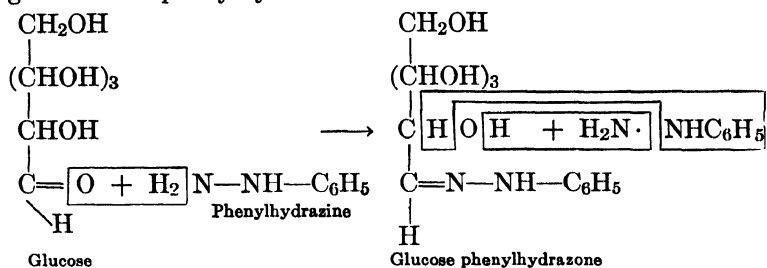
Glucose forms a cyanohydrin with HCN:



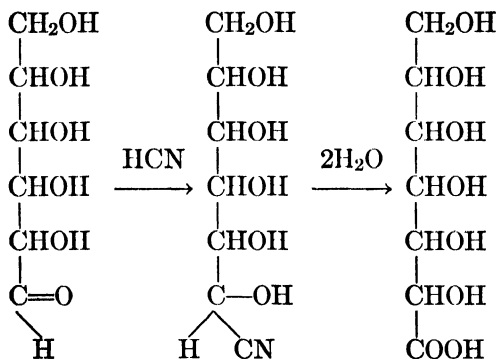
and an oxime with hydroxylamine,  $\text{NH}_2\text{OH}$ :



proving the presence of a carbonyl,  $\text{>CO}$ , group (see p.73). The presence of this group may be further shown by the reaction of glucose with phenylhydrazine:



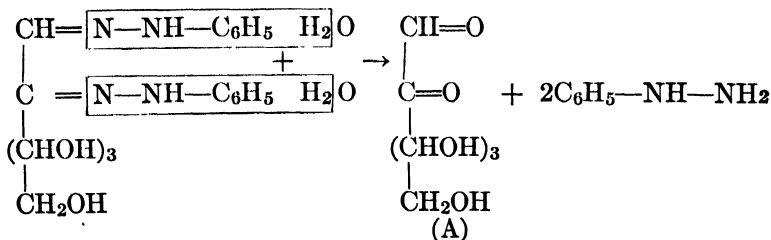
It now merely remains to determine the position of the CO group. This can be done in the following way: glucose is combined with HCN and the resulting product hydrolyzed (see p. 88).



The hydroxy acid is a normal, seven-carbon compound. The COOH group must be attached to the sixth carbon atom, and this, in turn, must have contained a CO group to have reacted with HCN. But the sixth carbon atom in glucose is the end carbon atom; therefore, the position of the CO group in glucose must be at the end carbon atom.

If we have gone into the constitution of glucose at some length, it is merely to illustrate the methods used in assigning formulas to the various carbohydrates.

The **osazone** formed when glucose and phenylhydrazine are brought together (p. 169), undergoes a very interesting transformation when warmed with concentrated hydrochloric acid:



(A) is known as **glucosone** and is as an example of a class of compounds called **osones**.

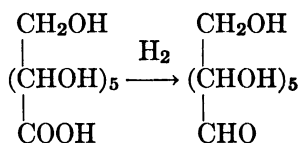


By reducing glucosone we change the aldehydic into an alcoholic group and get



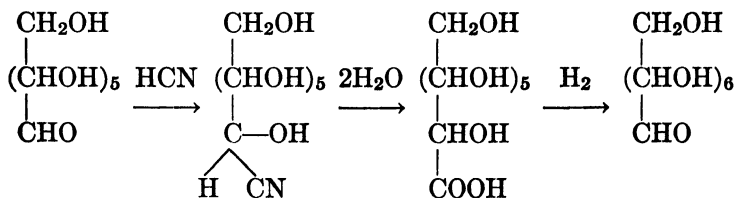
which, as may readily be seen, is a compound isomeric with glucose, but different from it in having a keto instead of an aldehyde group. This compound is none other than fructose (see p. 177). So that by means of the osone reaction we can pass from glucose to fructose. (Aldose  $\rightarrow$  Ketose.)

We have seen how by the use of HCN we can pass from a six to a seven carbon compound (p. 170). Now it is possible to reduce such a compound:



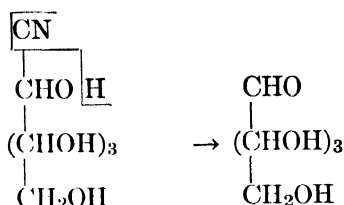
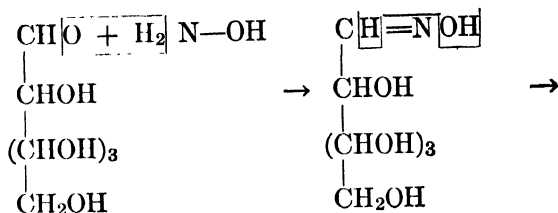
and obtain a product analogous in constitution to glucose except that it contains seven instead of six carbon atoms.

It is evident that this new compound may again be treated with HCN and the various steps repeated:

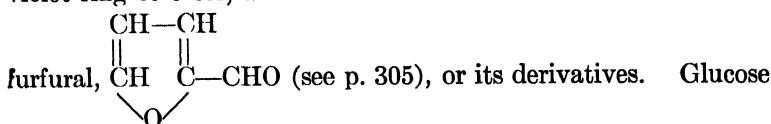


thereby obtaining an eight-carbon compound. Obviously, we have here a method by which the carbon content of a sugar may be *increased*—a very important process in synthetic chemistry.

An equally important and interesting procedure is to *decrease* the carbon content of a compound. This is done by first forming the oxime with hydroxylamine, then converting the product into the nitrile (by loss of water), and finally, by treatment with ammoniacal silver nitrate solution, splitting off HCN:

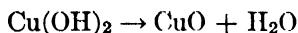


**Properties of Glucose.**—Like all carbohydrates, glucose reacts with the *Molisch* reagent ( $\alpha$ -naphthol) and conc.  $\text{H}_2\text{SO}_4$  to give a violet ring or color, a reaction said to be due to the formation of



forms an osazone with phenylhydrazine, a reaction already discussed. These osazones are of the utmost importance in the identification of a number of sugars, since they show definite crystalline forms and have definite melting points. Owing to the presence of the CHO group, glucose reduces ammoniacal silver solutions and the alkaline solutions of a number of metals, such as copper, bismuth and mercury. The best known of these reactions is the **Fehling's test**, which consists in heating glucose with a solution of copper sulfate, to which potassium hydroxide and Rochelle salt have been added; a yellowish red precipitate of cuprous oxide is obtained. (The theory of the reaction may be explained thus: in the absence of a reducing agent, such as glucose,

the cupric hydroxide that is first formed would be converted to black cupric oxide:

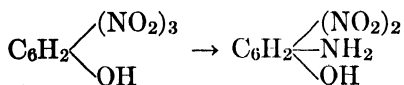


but when glucose, or any other appropriate reducing agent is present, cuprous oxide,  $\text{Cu}_2\text{O}$ , which is yellow to red in color, is formed instead:



Benedict has modified the Fehling reagent by mixing the copper sulfate with sodium citrate and sodium carbonate, producing a reagent which does not deteriorate even after long standing. The Benedict modification also has the advantage over Fehling's solution in that, when it is applied to test for glucose in the urine, neither uric acid nor creatinine—nitrogenous substances present in the urine—interfere with the test; nor does chloroform, which is often used as a preservative for the urine.)

Heated with picric acid, in the presence of KOH, glucose gives a red color—a reaction which forms the basis for a colorimetric determination of glucose in blood. (The reaction is said to be due to the reduction of picric (p. 280) to picramic acid;

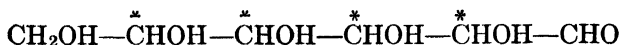


though the question has not been definitely settled.)

Yeast "ferments" glucose forming ethyl alcohol and  $\text{CO}_2$ :



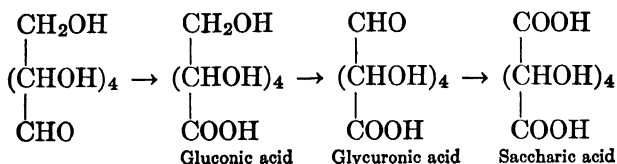
Glucose is optically active, turning the plane of polarized light to the right. If its formula be examined, it will be seen that glucose contains four asymmetric carbon atoms:



From the number of asymmetric carbon atoms in a compound, we can, with the help of a simple equation supplied by van't Hoff, calculate the possible number of isomers. The equation is  $A = 2^n$ , where  $A$  represents the number of isomers and  $n$  the number of asymmetric carbon atoms. Applying this equation to glucose,  $A = 2^4 = 16$ ; or there should be in all 16 possible stereoisomers. So far, no less than 14 of these have been isolated.

Glucose (both in the solid and in the form of syrup, as corn syrup) is used extensively in making confectionery, jellies, preserves, as table syrups, in the manufacture of alcoholic beverages, as a diluent (to increase bulk and weight) for dyes, in chewing gum, tobacco, etc.

On oxidation, glucose may give rise to the following products:

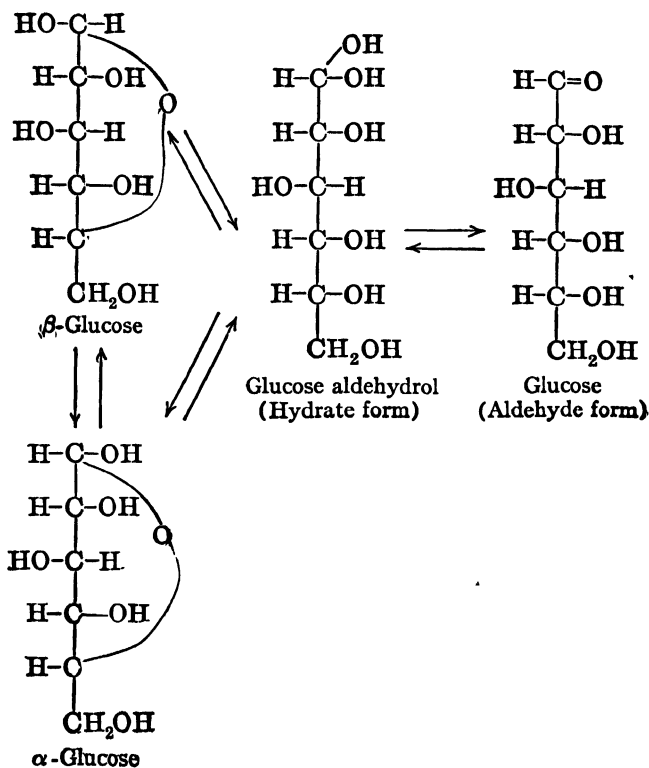


(Gluconic acid is now made by the electrolytic oxidation of glucose and also by the action of *Penicillium luteum purpurogenum* on glucose.)

(Glycuronic acid is of importance physiologically, since it may combine with poisonous substances, such as phenol, chloral, etc., to make them inert.)

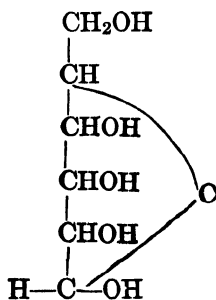
The optical activity of freshly prepared glucose solution diminishes on standing. This "mutarotation," as it is called, is due to the fact that there are, in reality, two forms of glucose,  $\alpha$ - and  $\beta$ -glucose present, having different rotatory powers, and the optical activity of the resulting mixture will depend upon the amounts of each present. This view is further strengthened by the fact that two isomeric methyl glucosides are known (p. 176), one of them,  $\alpha$ -methyl glucoside, yielding on hydrolysis one form of glucose ( $\alpha$ -glucose), and the other,  $\beta$ -methyl glucoside, yielding on hydrolysis the other form of glucose ( $\beta$ -glucose). The optical rotation of the two forms of glucose varies widely, the  $\alpha$  form being  $+109^\circ$  and the  $\beta$  form  $+22^\circ$ . If a solution of either form is allowed to stand, the rotation slowly changes and finally comes to an equilibrium at  $52.5^\circ$ .

These changes of glucose may be explained by the following changes:

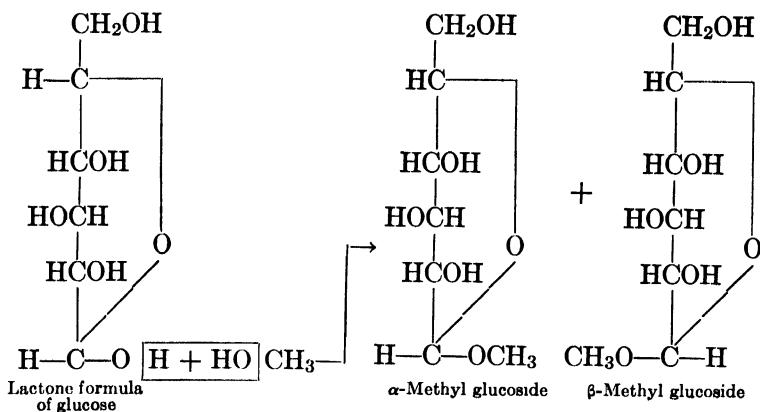


These facts, together with the additional fact that glucose is really not so reactive a compound as the usual structural formula indicates, has led to the conception of the *lactone structure* for the compound. This depends upon the possibility that a hydroxy compound of the glucose type may form an *amylen oxide ring*.

Besides the amylen oxide configuration, we may also have the ethylene, propylene or butylene oxide ring (1 : 2, 1 : 3, 1 : 4 ring). These types are collectively known as "gamma sugars," and they are more reactive than the 1 : 5 or amylen oxide sugar. One theory has it that a function of insulin (see p. 361) is to change the relatively stable 1 : 5 sugar into one of the more reactive gamma sugars.



**Glucosides.**—When glucose reacts with methanol in presence of HCl, two compounds,  $\alpha$ - and  $\beta$ -methyl glucosides, are obtained, the formulas of which may be represented thus:



The two glucosides have different physical properties. They also behave differently towards enzymes. Maltase hydrolyzes the  $\alpha$ - variety, but not the  $\beta$ -, and emulsin hydrolyzes the  $\beta$ -, but not the  $\alpha$ -.

The naturally occurring glucosides belong to the  $\beta$ -form. On hydrolysis, glucose and other products are produced. The following glucosides occur in nature: phloridzin, found in the bark of fruit trees, which yields fructose and phloroglucinol when hydrolyzed. Phloridzin is often used to induce a form of diabetes

in animals. Salicin,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{O} \cdot \text{C}_6\text{H}_{11}\text{O}_5 \\ \text{CH}_2\text{OH} \end{array}$ , on hydrolysis yields glu-

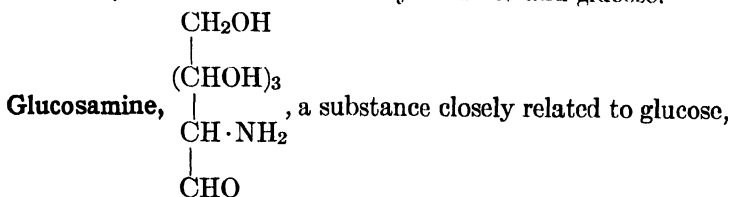
cose and saligenin, or salicyl alcohol. Salicin occurs in willow

bark. Amygdalin,  $\text{C}_6\text{H}_5 \cdot \text{CH} \begin{array}{l} \text{CN} \\ \text{O} \cdot \text{C}_{12}\text{H}_{21}\text{O}_{10} \end{array}$ , hydrolyzes to two molecules of glucose, HCN and benzaldehyde. It is found in

bitter almonds. Arbutin,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{O} \cdot \text{C}_6\text{H}_{11}\text{O}_5 \\ \text{OH} \end{array}$ , hydrolyzes to glu-

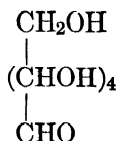
cose and hydroquinone. It is present in the leaves of the berry tree. Indican, present in the indigo plant, hydrolyzes into glucose and indoxyl, which rapidly oxidizes to indigo. Myronic acid is present in black mustard seed. On hydrolysis, it is con-

verted to dextrose,  $\text{KHSO}_4$  and allyl isothiocyanate ( $\text{C}_3\text{H}_5\cdot\text{NCS}$ ). Ruberythric acid is present in madder root. On hydrolysis or fermentation, it is converted to the dye alizarin and glucose.



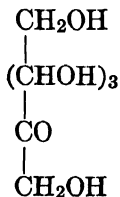
is an important constituent of glycoproteins, such as mucin and the various mucoids, and may be obtained from them by hydrolysis. It is also present in chitin, a constituent of the shells of the lobster. Glucosamine reduces Fehling's solution, and its general properties are much like those of glucose.

**Galactose** is an aldohexose, like glucose:



It is obtained by the hydrolysis of lactose or milk sugar. It is also an important constituent of the cerebrosides of the brain. Like glucose, it forms an osazone with phenylhydrazine (differing, however, in structure), and reduces Fehling's solution, but ferments slowly with yeast. On oxidation, it forms mucic acid (stereoisomer of saccharic acid), which also differentiates galactose from glucose.

**Fructose**, or levulose, or fruit-sugar, found in honey, has the formula:

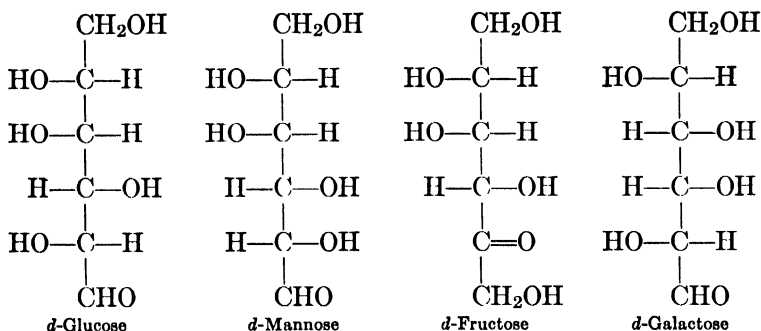


and is, therefore, a ketohexose, isomeric with glucose and galactose. Fructose, glucose and galactose are, physiologically, the three important hexoses. Fructose may be obtained by hydrolysis of

cane sugar or sucrose. Like the other two common hexoses, fructose reduces Fehling's solution and forms an osazone. The osazone with phenylhydrazine is the same as the one formed with glucose. It may be distinguished from glucose and galactose by the *Seliwanoff* test, which consists in heating fructose with resorcinol dissolved in dilute HCl, whereby a red color and a red precipitate are obtained. Fructose is 50 per cent sweeter than sucrose. A method has recently been proposed to prepare fructose in large quantities from the Jerusalem artichoke.

*i*-Fructose,  $C_6H_{12}O_6$ , is obtained by polymerization of six moles of formaldehyde with calcium hydroxide. A mixture of sugars is obtained known as "formose" from which *i*-fructose has been isolated. *i*-fructose is the racemic (*dl*) form.

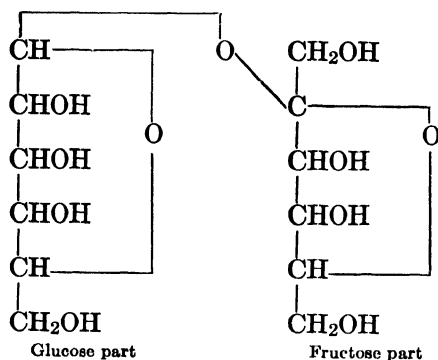
The stereo-configuration of four of the hexoses can be shown by the following formulas:



What differences do you notice in these formulas?

**Sucrose**, or cane sugar,  $C_{12}H_{22}O_{11}$ , is one of three physiologically important disaccharides, the other two being, lactose and maltose. On acid hydrolysis, sucrose yields a mixture of glucose and fructose ("invert sugar"). The same result is brought about by the enzyme *sucrase*, found in the small intestine. On a large scale, sucrose is obtained from sugar-cane, sugar-beet, etc. Unlike dextrose, fructose, galactose, maltose and lactose, five other important sugars, it does not reduce Fehling's solution, nor does it form an osazone—that is, it does not behave like an aldehyde or ketone sugar. To explain this, the suggested formula for sucrose does not contain a "free" CO group:

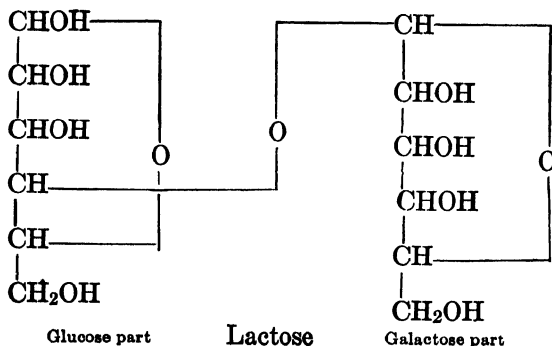




A recent noteworthy achievement has been the synthetic production of sucrose in the chemist's laboratory. Pictet has accomplished this by combining the tetraacetate of glucose with the tetraacetate of gamma-fructose. The octaacetate of sucrose so formed was hydrolyzed under pressure, giving sodium acetate and sucrose.

When sugar is heated above its melting-point, caramel is formed. This is a brown substance and is used extensively as a coloring material in food preparations.

(Whether the sugar is obtained from the sugar-cane or the sugar-beet, the principle involved in the extraction process consists in first separating the juice from the insoluble fiber, next in precipitating albuminous material and neutralizing the acids present, and finally in evaporating the filtrate and separating the crystals from the mother-liquor. The latter contains some 50 per cent of sucrose and is known as "molasses," a product used in the making of alcohol. If the "molasses" is derived from the sugar-cane, it may be used as table syrup and in the preparation of rum.)



**Lactose**,  $C_{12}H_{22}O_{11}$ , or milk sugar, occurs in milk to the extent of about 4 per cent. On hydrolysis, or by the action of the enzyme lactase in the small intestine, it yields glucose and galactose. Since it reduces Fehling's solution and forms an osazone, we assume that it contains a "free" CO group. (See formula on bottom of page 179.)

**Maltose**,  $C_{12}H_{22}O_{11}$ , or malt sugar, is found in malt, which is the sprouted grain of barley. This sprouted grain contains an enzyme, diastase, which converts the starch in the grain into maltose. A similar action occurs in the body when the enzyme ptyalin, found in saliva, acts on the starch in foods. When maltose is hydrolyzed by acids, or by maltase (an enzyme found in yeast and also in the small intestine) two molecules of glucose are obtained. (The maltase in yeast, acting on maltose, forms glucose, and then the zymase in yeast, acting on glucose, produces ethyl alcohol and  $CO_2$ .) Maltose behaves similarly to lactose, but the latter forms galactose as one of its products of hydrolysis, whereas maltose forms only glucose.

**Raffinose**,  $C_{18}H_{32}O_{16}$ , is a trisaccharide occurring in cotton seed, etc. It does not reduce Fehling's solution. On hydrolysis, it yields fructose, glucose and galactose. This hydrolysis may either be brought about by acids or by certain bacteria and yeasts.

**Chitin**, a tetrasaccharide, is probably composed of four glucosamine (p. 177) units. It is prepared from the shells of lobsters or crabs.

**Chondroitin**, another tetrasaccharide, is contained in cartilage, often in combination with protein.

**Starch**, one of a number of polysaccharides having the general formula  $(C_6H_{10}O_5)_x$ , is widely distributed in the vegetable kingdom. It is synthesized in the plant by the combined action of carbon dioxide and water in the presence of chlorophyll. It is hydrolyzed in the body first to soluble starch, then to a number of dextrans, then to maltose and finally to glucose, and in the latter form is absorbed into the blood stream. Boiled with water, the granules swell and burst, and "starch paste" is obtained. Starch gives a blue color with iodine.

**Dextrins** of the general formula  $(C_6H_{10}O_5)_x$ , are considered somewhat less complex than starch itself, for the dextrans are obtained in the course of the hydrolysis of starch by enzymes.

Erythrodextrin gives a reddish-brown color with iodine and achrodextrin fails to give any color.

**Glycogen**, or "animal starch" ( $C_6H_{10}O_5$ )<sub>x</sub>, is found almost exclusively in the animal kingdom, and particularly in the liver. It is the form in which carbohydrate is stored in the body. With iodine it gives a red color.

**Inulin** is a polysaccharide found in the tubers of the artichoke, dahlia, etc. Unlike starch, it is soluble in hot water and gives a negative reaction with iodine. On hydrolysis, it yields the monosaccharide levulose.

✓ **Cellulose**, ( $C_6H_{10}O_5$ )<sub>x</sub>, is the chief constituent of the cell wall of plants. Cotton fiber is almost pure cellulose, or "normal" cellulose. When hydrolyzed, cellulose yields glucose. Lignocellulose is probably a combination of cellulose with gums and resins, while pectocellulose is a combination of cellulose and a substance, pectin, the latter being responsible for the formation of jellies from fruit.

Cellulose is, chemically, highly inert. It may be dissolved (possibly with some changes) in *Schweitzer's* reagent (ammoniacal solution of copper oxide).

Acetyl derivatives may be obtained with glacial acetic acid, and acetic anhydride, showing cellulose to contain OH groups.

Industrially, cellulose is of immense importance. It is the chief ingredient of cotton, linen, hemp, etc., and of paper (which in turn, may be made from cotton and linen rags or from wood). Parchment paper is cellulose treated with conc. sulfuric acid. Mercerized cotton is cotton treated with sodium hydroxide solution, whereby the cotton is converted into a stronger fiber with a glossy appearance somewhat resembling silk. It takes dyes more readily than cotton.

Rayon, or as it was called for a time, *artificial silk*, is manufactured in one of four different ways. In the nitrocellulose process, the cotton linters are treated with a mixture of nitric and sulfuric acids, and the nitrocellulose so obtained is dissolved in alcohol and ether. The solution is then forced by pressure through capillary glass tubes and, by the application of blasts of hot air, the filaments which form, solidify. These filaments are still nitrocellulose in composition and highly flammable. The nitro group is therefore removed by treatment with sodium hydrosulfide. In the cuprammonium process, the linters or wood pulp are mixed with

copper hydroxide and the mixture dissolved in concentrated ammonia. The solution is forced through fine holes into a bath of caustic soda or sulfuric acid, thereby causing the filaments to coagulate. In the *acetate process* the linters are treated with acetic anhydride, glacial acetic acid and sulfuric acid also being present. The cellulose acetate so formed is precipitated with water and dissolved in acetone. The viscous solution is now forced under pressure through the capillary tubes to give rise to the fine filaments which, when spun in groups and twisted, gives rise to a yarn known in the trade as "Celanese" and "Lustron." Unlike the other varieties of rayon, which are really pure cellulose, this product is really cellulose acetate.

Cellulose acetate is more stable to heat and light than is cellulose nitrate. The former is now extensively used in the manufacture of non-inflammable photographic films, cellulose plastics, non-shatterable glass, phonograph records, lacquers, transparent wrappers, etc.

The method most commonly used in the preparation of rayon is the *viscose process*, a process by which 80 per cent of the total world's production of rayon is made. Spruce pulp or cotton linters are soaked in an 18 per cent caustic soda solution, thereby causing a swelling of the fibers and the production of a compound known as soda-cellulose. The soda-cellulose is next treated with carbon disulfide forming a product known as cellulose xanthate, which, unlike the cellulose, is a water-soluble compound, and which is known as "viscose." The solution is forced through fine holes and into sulfuric acid, the filaments so formed consisting of regenerated cellulose. In this process, as in the other three, the filaments are finally converted into skeins of twisted yarn. Here, as in the other processes, the skeins are bleached with chlorine. (In the viscose process, sulfur impurities arising from the use of carbon disulfide are removed by treatment with sodium sulfide prior to bleaching with chlorine.)

Within a generation rayon has taken a commanding place in the textile industry and is finding applications in all phases of the textile trade.

With nitric acid, cellulose forms various nitrate compounds. The higher nitrates (hexanitate), such as gun-cotton (soluble in alcohol-ether-mixture), are explosives; and the lower nitrates are used in the manufacture of celluloid. Pyroxylin, a mixture



of lower cellulose nitrates, is used in preparing lacquers and making rayon and celluloid. It is soluble in amyl acetate and methanol.

An important product containing pyroxylin is known under the name of "Duco" and is used very extensively as a lacquer finish. The pyroxylin is dissolved in amyl acetate or other solvents, and small amounts of gums or resins are added, producing a lacquer. By the addition of finely ground pigments, pyroxylin enamels are produced. When a lacquer film is exposed to the air the solvents, which have acted as a vehicle for the pyroxylin, gums, pigments, immediately begin to evaporate, and in a short time a hard, tough film is produced. Linseed oil and other vegetable oil paints dry by air oxidation while the pyroxylin lacquers dry entirely by evaporation. Collodion, similar to pyroxylin in composition, is used for photographic films, as a protective covering for wounds, etc., and in the making of dialyzing bags. It is soluble in an alcohol-ether mixture. Celluloid is made by subjecting pyroxylin and camphor to heat and pressure. Cordite, a smokeless powder, is made by treating gun-cotton and nitroglycerine with acetone and some vaseline.

*Mannans, Galactans, Hemicellulose, etc.*—These substances, present in the seeds of numerous plants, resemble cellulose, but dissolve in dilute alkali and on hydrolysis yield not only glucose (as cellulose does) but other hexoses as well. Agar-agar is a galactan which yields galactose on hydrolysis. Mannans, as their name implies, yields mannose when hydrolyzed.

*Gums, Pectins, Mucilages.*—These are also polysaccharides containing pentose and hexose groups. The gums are probably carbohydrates combined with acids. Some are soluble, and others insoluble in water. Gum arabic, gum tragacanth, etc., are used as vehicles to suspend insoluble substances in aqueous emulsions. Mucilages form "viscous" liquids with water. The gelatinization of fruit extracts is due to the pectin present.

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## CHAPTER XVIII

### FOODSTUFFS AND THEIR CHANGES IN THE BODY

THE foodstuffs may be divided into carbohydrates, fats, proteins, mineral salts, water and vitamins. Some include oxygen in the list because of the very necessary part it plays in the oxidation of the foodstuffs in the body. We may dismiss the mineral salts, water and vitamins, because, so far as we know, they undergo no chemical changes preparatory to their absorption by the blood and tissues. We will confine ourselves to the carbohydrates, fats and proteins, because they do undergo profound chemical changes in the digestive tube and after they have left the digestive tube and enter the liver and various tissues of the body.

The fats and carbohydrates are ultimately oxidized to carbon dioxide and water, and eliminated as such. The proteins, aside from being oxidized to carbon dioxide and water, also form a number of nitrogenous products which appear chiefly in the urine, such as urea, uric acid, creatinine, etc. These nitrogenous products really represent incomplete stages in the oxidation of the protein, for the complete oxidation of protein would yield carbon dioxide, water and nitrogen.

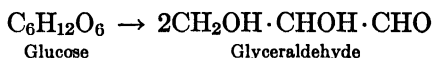
Complex substances of the types of fats, proteins and carbohydrates are not immediately oxidized in the body to carbon dioxide, water, and relatively simple nitrogenous substances; there must be a number of intermediate steps in the process. During the past few years, organic and physiological chemists have been very busy tracing these steps. While there is still much to be elucidated, much has already been done, and a brief résumé of the work accomplished will be given here. For those desiring a more detailed account we must refer them to the references at the end of the chapter, particularly to Dakin's masterly monograph.

**Carbohydrates.**—The digestible carbohydrates are all broken down to monosaccharides before absorption. The enzyme

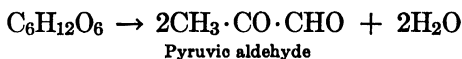


ptyalin (in saliva), amylopsin (in pancreatic juice), sucrase, maltase and lactase (in intestinal juice) hydrolyze the more complex carbohydrates to the hexoses,—glucose, levulose and galactose (p. 167). These are then absorbed through the walls of the small intestine, pass into the blood, thence to the liver, and there are synthesized to glycogen (p. 181) and stored as such. Whenever fuel is needed by the body, the glycogen reserve is called upon, and the glycogen is hydrolyzed to glucose, but this time to glucose only. Then this glucose is oxidized in the tissues to—ultimately—carbon dioxide and water.

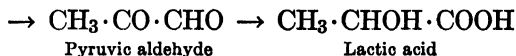
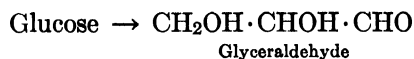
It is believed that the first step in the oxidation of glucose is the splitting of the glucose molecule into two three-carbon molecules. It was believed at one time that the most probable three-carbon compound to be formed was lactic acid, since this substance is always produced by working muscle; but the view more generally held now is to regard either glyceraldehyde,  $\text{CH}_2\text{OH}\cdot\text{CHOH}\cdot\text{CHO}$ , or pyruvic aldehyde (methyl glyoxal)  $\text{CH}_3\cdot\text{CO}\cdot\text{CHO}$ , as the first step in the decomposition of glucose, and lactic acid as a by-product obtained either from glyceraldehyde or pyruvic aldehyde. So that we may represent the first steps thus:



or



and lactic acid could then be formed in one of two ways:

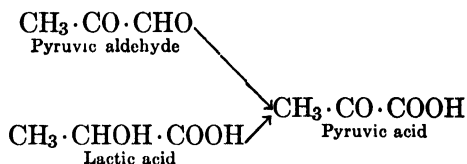


or, still better,

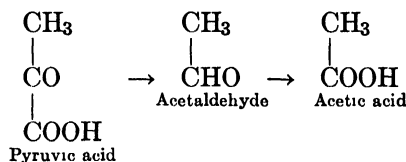


(The action of alkali on glucose has been shown to yield the products mentioned in these reactions. Further, using surviving liver tissue, it has been possible to convert both pyruvic aldehyde and glyceraldehyde into lactic acid; and in diabetes, where the mechanism of the cell is disturbed, glyceraldehyde, pyruvic aldehyde and lactic acid have all been shown to produce glucose.)

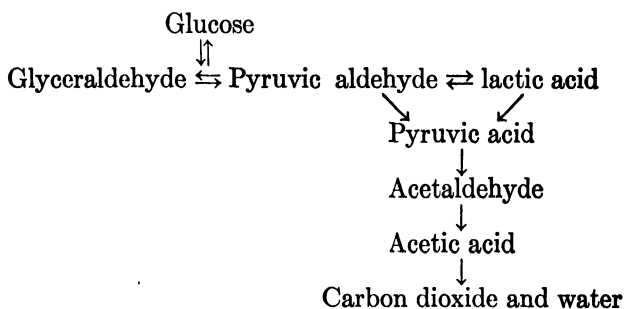
True oxidation probably comes into play at this point; that is to say, with the conversion of either pyruvic aldehyde, or lactic acid, into pyruvic acid;



Now it has been shown that in the organism,  $\alpha$ -ketonic acids (of which pyruvic acid is an example) are changed into the fatty acid with one less carbon atom; in this case into acetic acid. It seems probable that the intermediate step here is acetaldehyde. (In this connection, it may be mentioned that yeast juice ferments pyruvic acid into acetaldehyde and carbon dioxide.) So that the steps are probably



The acetic acid is finally oxidized to carbon dioxide and water. Summarizing the various steps:



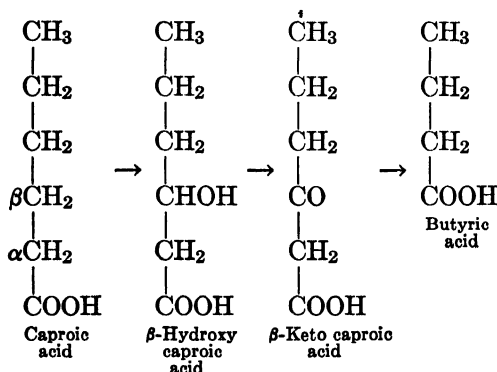
**Fats.**<sup>1</sup>—The straight fats, that is to say the glyceryl esters of stearic, palmitic and oleic acids (p. 105), are hydrolyzed in the digestive tract into glycerol and fatty acids. (Some fatty acid

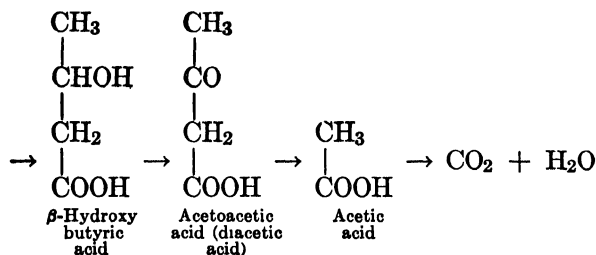
<sup>1</sup> The lipoids, such as lecithin and cholesterol (p. 110) often associated with fat in food, undergo changes in the body which are either too complex, or too little understood to be discussed here.

is also converted into soap, due to the alkalinity of the medium.) This is mainly brought about by the enzyme lipase (in the pancreatic juice), which, in turn, is very actively assisted by the "bile salts," the sodium glycocholate and sodium taurocholate (found in bile). The fatty acids and glycerol, immediately after absorption through the walls of the small intestine, are synthesized back again into fats, and as such pass from the lacteals into the lymph, into the thoracic duct, and thence into the general circulation. The fat not needed for immediate use is largely stored in the adipose tissues.

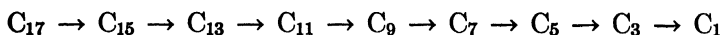
The preliminary step in the oxidation of fats is probably one of hydrolysis into glycerol and fatty acid. It may be assumed that the glycerol is first oxidized to glyceraldehyde, which would then, of course, follow the usual scheme of carbohydrate oxidation (p. 187). The oxidation of the fatty acid part of the molecule probably takes place in accordance with a theory first advanced by Knoop and known as Knoop's " $\beta$ -oxidation theory." According to this view, the fatty acid is first attacked in the  $\beta$ -position, being changed to a hydroxy and then to an oxy (keto) acid. The  $\alpha$  and  $\beta$  carbon atoms (with their hydrogen atoms) are probably next oxidized to carbon dioxide and water, leaving a fatty acid containing two less carbon atoms. Then the process is repeated until finally carbon dioxide and water are produced. At each stage of the process, two carbon atoms are removed, so that, if we start with stearic acid, containing  $C_{18}$  atoms, we pass to palmitic,  $C_{16}$ , then to  $C_{14}$ , etc.

To illustrate the process, let us assume, that we have reached the  $C_6$  stage with caproic acid. The changes can be illustrated as





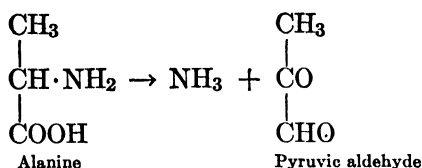
In diabetes, the poisonous "acetone bodies" or "acid bodies" which are so often produced, are derived from fats. These "acetone bodies" include butyric acid,  $\beta$ -hydroxybutyric acid, acetoacetic acid and acetone. The acetone is a by-product obtained probably from acetoacetic acid by the loss of  $\text{CO}_2$ . It would seem as if the diabetic has not only difficulty in oxidizing glucose, but also in completely oxidizing fats; the fats in his case are oxidized to the four-carbon stage and no further. Kahn, working with the knowledge that the naturally-occurring fats all contain an even number of carbon atoms, and stimulated by Knoop's theory that fatty acids are oxidized in such a way as to lose two carbon atoms at each stage, has synthesized an odd-carbon fat—from margaric acid,  $\text{C}_{16}\text{H}_{33}\cdot\text{COOH}$ , a  $\text{C}_{17}$  acid—which, when given to the diabetic, is said not to produce "acetone bodies," because in the oxidation of this odd-carbon fat, the four-carbon acids are avoided; thus



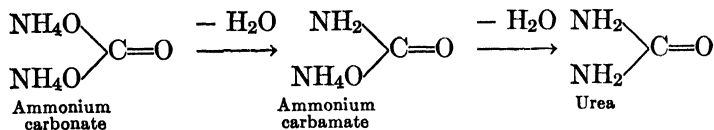
**Proteins.**—The proteins<sup>1</sup> are hydrolyzed in the digestive tract by the enzymes pepsin (in gastric juice), trypsin (in pancreatic juice) and erepsin (intestinal juice). The final hydrolytic products are amino acids (p. 152). The amino acids are absorbed as such, and either finally pass into the tissue to form tissue protein, probably in some such way as outlined in Fischer's synthesis of polypeptides from amino acids (p. 151), or are eliminated principally in the form of urea, by a process of "de-amination," which occurs very largely in the liver, but may also occur in other tissues. This process of "de-amination" is essentially the splitting off of the  $\text{NH}_2$  group from the amino

<sup>1</sup> We refer here to the "simple" proteins (p. 149). The "conjugated" proteins (p. 150) present many difficulties.

acid. Dakin has shown that an  $\alpha$ -amino acid, in water, undergoes spontaneous dissociation into the corresponding  $\alpha$ -ketonic aldehyde and ammonia; so that if we take alanine as an example of an  $\alpha$ -amino acid, we would get

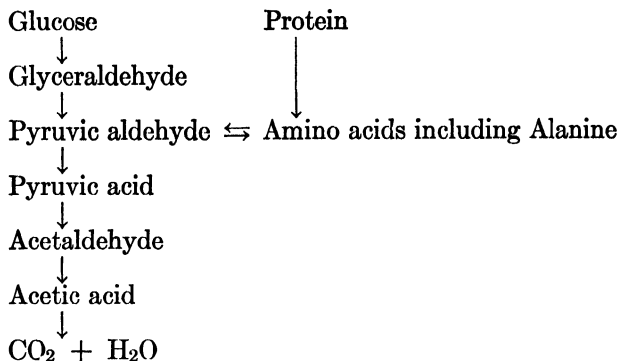


The pyruvic aldehyde would then most probably be further oxidized according to the scheme outlined under carbohydrates. (This, by the way, explains how proteins may also serve as a source of energy; and it also suggests how, in cases of diabetes, the carbohydrate is formed from protein.) The ammonia combines with carbonic acid, a constant product of metabolism, to give ammonium carbonate, which, by a process of dehydration, is finally converted into urea:

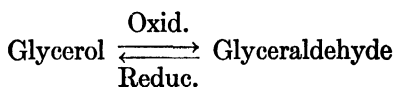


It has already been mentioned that in the urine we find nitrogenous products other than urea. Since protein is the only one of the three classes of foodstuffs which contains the element nitrogen, it is reasonable to assume that these nitrogenous products are of protein origin. Even under normal conditions a small quantity of ammonia (in the form of ammonium salts) is eliminated. We also find uric acid and purine bases, which are obviously derived from the nucleoproteins of the food (or body tissues) and the purine substances, such as are found in meat, for example (see p. 156). An appreciable amount of creatinine, and, to a less extent, creatine (see p. 121), is also found in the urine.

**The probable interrelationships of protein, fat and carbohydrate in the body.**—The connecting links between protein and carbohydrate have already been indicated. They will be shown schematically here:

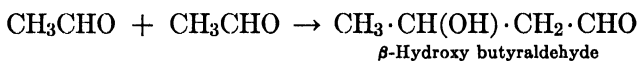


What are the connecting links between fats and carbohydrates? How are we to explain that an excess of carbohydrate is so easily deposited in the form of fat? The glycerol part of the fat is obviously connected with the glyceraldehyde from glucose:



But how are we to suggest the possible formation of a complex fatty acid from the glucose molecule?

It has been suggested that the synthesis may be along the lines of an aldol condensation (p. 80). Starting with acetaldehyde, a product formed in the oxidation of glucose, two molecules of the aldehyde may condense to give:

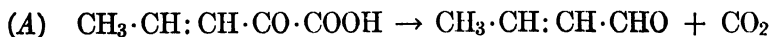


which may then combine with another molecule of acetaldehyde to give a 6-carbon compound, and so on, until the C<sub>16</sub> or C<sub>18</sub> is reached. By simultaneous reduction and oxidation, or the transfer of the oxygen attached to the *β*-carbon to the end carbon, the hydroxy aldehyde may be converted to the normal, saturated acid.

Another theory, largely due to Miss Smedley, and based on sound experimental evidence, may be summarized as follows: Pyruvic acid and acetaldehyde—both products formed in the oxidation of glucose—condense thus:

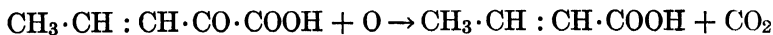


The ketonic acid is next converted into its aldehyde and carbon dioxide in a manner similar to the conversion of pyruvic acid to acetaldehyde (p. 188).



This aldehyde has two more carbon atoms than the acetaldehyde with which we started; it now condenses with another molecule of pyruvic acid, forming a ketonic acid with more carbon atoms; and so on.

The oxidation of the unsaturated ketonic acid (A) yields an unsaturated acid with one less carbon atom:



By reduction we obtain a fatty acid containing two more carbon atoms than the aldehyde from which we started.

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## CHAPTER XIX

### SULFUR, PHOSPHORUS, ARSENIC AND ORGANO-METALLIC COMPOUNDS

#### SULFUR COMPOUNDS

SULFUR is just below oxygen in the periodic table, and the two elements should, therefore, show close relationships. We find abundant evidence of such structural relationships in organic chemistry. An entire series of analogous compounds may be formed by substituting sulfur for oxygen in organic compounds.



Alcohol



Mercaptan or  
thioalcohol



Methyl mercaptan or  
methyl thioalcohol

They are called mercaptans for they combine with mercury compounds (*corpus mercurium captans.*).



Alcoholate



Thioalcoholate  
or  
mercaptide



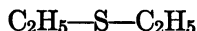
Sodium ethyl mercaptide



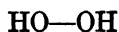
An ether or  
alkyl oxide



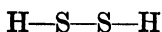
Alkyl sulfide  
or  
a thioether



Ethyl sulfide  
or  
ethyl thioether



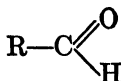
or  
 $\text{H}_2\text{O}_2$



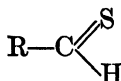
or  
 $\text{H}_2\text{S}_2$  as in  $\text{Na}_2\text{S}_2$



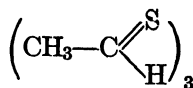
Organic disulfide



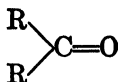
Aldehyde



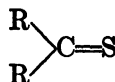
Thioaldehyde



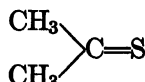
Trithioacetaldehyde



Ketone



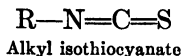
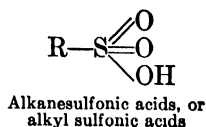
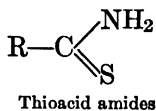
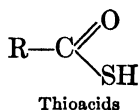
Thioketone



Thioacetone

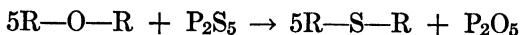


In addition to these types of compounds we have:



and others, showing in every case the close analogy of these sulfur compounds to the corresponding oxygen ones.

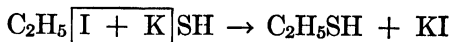
Many of these sulfur compounds may be prepared from their oxygen analogues by the use of phosphorus pentasulfide; e.g.,



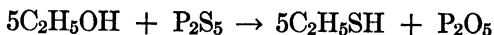
Most of the compounds having the structure  $\text{R}-\text{S}-\text{H}$  and  $\text{R}-\text{S}-\text{R}$  have exceedingly putrid disagreeable odors and are poisonous.

**Mercaptans** may be prepared:

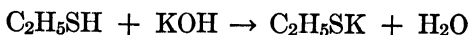
1. By the action of potassium hydrogen sulfide on the halogen compound: e.g.,



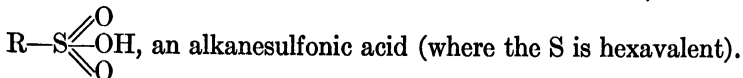
2. By the action of phosphorus pentasulfide on an alcohol; e.g.,



Mercaptans are converted to mercaptides thus:

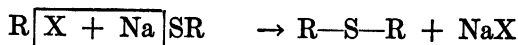


On oxidation,  $\text{R}-\text{S}-\text{H}$  (where the S is divalent) becomes



**Sulfides.**—These may be prepared:

1. By the action of a thioalcoholate on the halogen compound:



(Analogous to  $\text{R} \boxed{\text{X} + \text{Na}} \text{OR} \rightarrow \text{ROR} - \text{an ether} - + \text{NaX}$ )

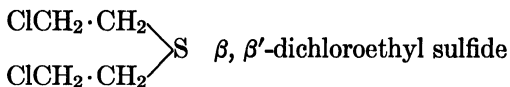
2. By the action of potassium sulfide on the halogen compound



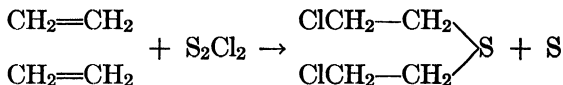
The thioethers on oxidation give, first,  $\text{R-S=O}$ , a sulfoxide  
and then  $\begin{array}{c} \text{R} \\ \diagup \\ \text{S} \\ \diagdown \\ \text{R} \end{array} \begin{array}{c} \text{O} \\ // \\ \text{O} \end{array}$ , a sulfone.

Mercaptans, sulfides, disulfides, etc., occur in petroleum.

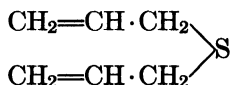
**Mustard gas** (one of the most toxic gases used in the late war)  
is



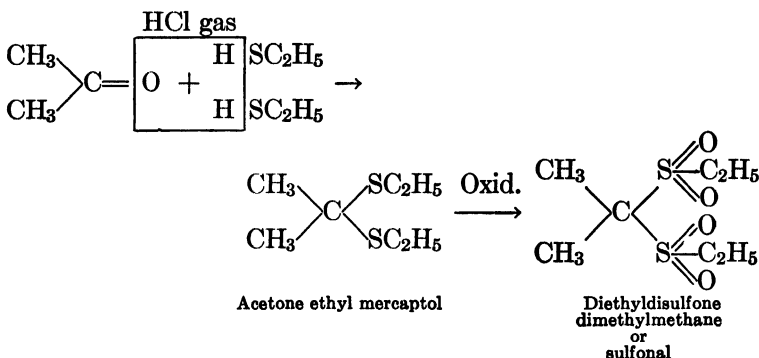
It was manufactured by passing ethylene into sulfur monochloride,



Oil of garlic contains allyl sulfide:

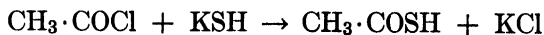


**Sulfonal** may be prepared from acetone by combining it with ethyl mercaptan in presence of a dehydrating agent and oxidizing the product with  $\text{KMnO}_4$ :



Sulfonal has hypnotic properties and is used as a soporific. Trional is the ethyl derivative in place of one methyl group. The starting substance for its synthesis is  $\text{C}_2\text{H}_5 \cdot \text{CO} \cdot \text{CH}_3$ .

**Thioacetic acid**,  $\text{CH}_3\text{COSH}$  is prepared by the following reaction:



**Sulfoacetic acid** is  $\text{CH}_2\begin{matrix} \nearrow \text{SO}_3\text{H} \\ \searrow \text{COOH} \end{matrix}$ .

**Trithioacetaldehyde**,  $(\text{CH}_3-\text{C}\begin{matrix} \nearrow \text{S} \\ \searrow \text{H} \end{matrix})_3$  and **thioacetone**,  $\text{CH}_3\begin{matrix} \nearrow \text{C}=\text{S} \\ \searrow \text{CH}_3 \end{matrix}$ , are prepared by the action of  $\text{H}_2\text{S}$  on acetaldehyde and acetone, respectively.

The alkane sulfonic acids (or alkyl sulfonic acids) of the type  $\text{R}-\text{S}\begin{matrix} \nearrow \text{O} \\ \searrow \text{OH} \end{matrix}$  are not of particular importance in the aliphatic series, but they are in the aromatic series.

**Taurine**, or  $\beta$ -amino ethanesulfonic acid,  $\begin{matrix} \text{CH}_2-\text{NH}_2 \\ | \\ \text{CH}_2-\text{S}\begin{matrix} \nearrow \text{O} \\ \searrow \text{OH} \end{matrix} \end{matrix}$ , is a

constituent of taurocholic acid, which in the form of its sodium salt is an important constituent of the bile.

**Xanthic acid**,  $\text{C}\begin{matrix} \nearrow \text{SH} \\ \searrow \text{OC}_2\text{H}_5 \end{matrix}$ , is the ethyl ester of dithiocarbonic acid. Cellulose xanthate  $(\text{C}\begin{matrix} \nearrow \text{SNa} \\ \searrow \text{O cellulose} \end{matrix})$  is produced when cellulose is heated with  $\text{CS}_2$  and  $\text{NaOH}$  solution. This is the basis for the "viscose" artificial silk. Thiourea,  $\text{C}\begin{matrix} \nearrow \text{NH}_2 \\ \searrow \text{NH}_2 \end{matrix}$ , is the sulfur analogue of urea,  $\text{C}\begin{matrix} \nearrow \text{NH}_2 \\ \searrow \text{NH}_2 \end{matrix}$ , which in turn is the principal nitrogen end product in the metabolism of proteins in the body. Allyl isothiocyanate,  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{N}=\text{C}=\text{S}$ , is present in mustard oil.

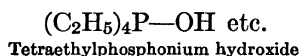
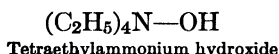
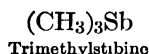
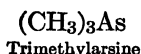
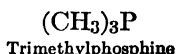
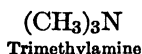
#### PHOSPHORUS AND ARSENIC COMPOUNDS

According to the periodic table, nitrogen, phosphorus, arsenic and antimony belong to the same family of elements. This implies that compounds of P, As and Sb, analogous to N com-

pounds, should exist. These do exist. We have, for example, in inorganic chemistry:

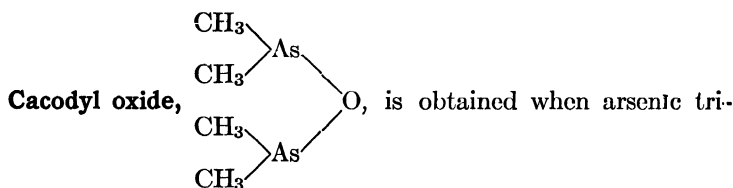


and in organic chemistry:



(The phosphorus compounds are, as a rule, more reactive than the corresponding nitrogen compounds).

(A number of proteins, such as the nucleoprotein found in the nucleus of cells, the casein in milk, and the phosphatides—of which the lecithin of egg yolk and brain tissue is an example—contain the element phosphorus as an integral part of a complex molecule.) (See p.110.)



oxide and potassium acetate are distilled:



The name **cacodyl**—"stinking"—was given to the group  $(\text{CH}_3)_2\text{As}$ —by Bunsen, its discoverer. The cacodyl compounds

are highly poisonous. The salts of cacodylic acid,  $(\text{CH}_3)_2\text{As} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{OH} \end{array}$ , as the sodium, calcium, iron and mercury cacodylates, are used in the treatment of syphilis, tuberculosis, malaria and pellagra.

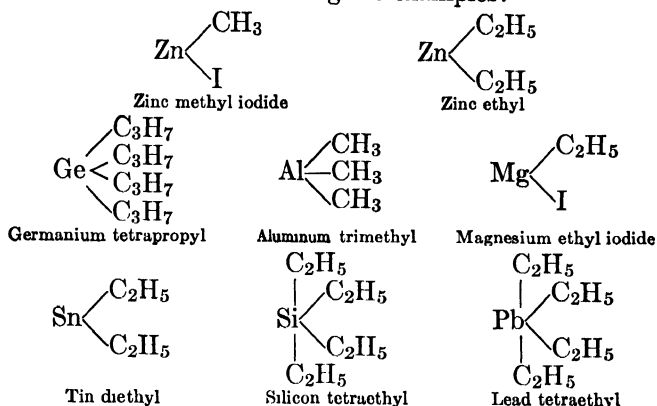
Ethyl dichloroarsine,  $\text{C}_2\text{H}_5\text{AsCl}_2$ , and  $\text{CH}=\text{CH} \cdot \text{AsCl}_2$ , chloro-  
 $\begin{array}{c} \text{Cl} \\ | \\ \text{CH}=\text{CH} \cdot \text{AsCl}_2 \end{array}$   
 vinyl dichloroarsine, known as "Lewisite"—were used as war gases.

The antimony compounds are similar in structure to those of arsenic.

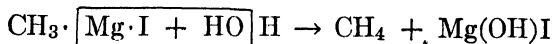
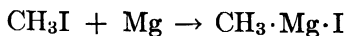
A number of very important arsenic compounds will be discussed under the aromatic series (p. 338).

## ORGANO-METALLIC COMPOUNDS

Various combinations of organic radicals with metallic elements are known. The following are examples:

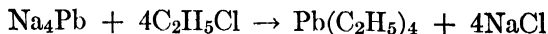


Compounds of the type  $\text{R}-\text{Mg}-\text{X}$ , are highly important, since they are extensively used in organic chemistry. Only a few examples are given.



For the preparation of secondary and tertiary alcohols see p. 55. Using the Grignard compounds, we can synthesize alcohols, ethers, aldehydes, ketones, acids, esters, nitriles, organo-metallic compounds, etc.

(Lead tetraethyl is used as the "anti-knock" compound in automobile engines. It may be prepared thus:



The product sold as "ethyl gas" is gasoline containing a small quantity of lead tetraethyl and carbon tetrachloride or ethylene dibromide.)

## READING REFERENCES

WREN—Organometallic Compounds of Zinc and Magnesium.

WEST AND GILMAN—Organomagnesium Compounds in Synthetic Chemistry. *National Research Council*, Washington, 1922.

NORRIS—The Opportunities for Research in Aliphatic Chemistry. *Industrial and Engineering Chemistry*, **18**, 262 (1926).

KRAUS—The In-Organic Side of Organic Chemistry. *Journal of Chemical Education*, **6**, 1478 (1929).

From now on compare the following chapters with the corresponding ones in the aliphatic series.

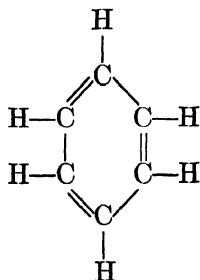
## CHAPTER XX

### INTRODUCTION TO CYCLIC COMPOUNDS

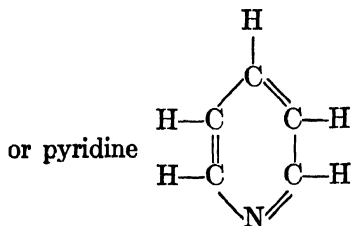
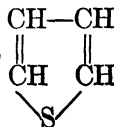
So far we have been studying the "open-chain," or "aliphatic" series of compounds. Now we are about to take up the "closed-chain" or "cyclic" compounds, which, in many respects possess properties differing from those of the aliphatic series.

The cyclic compounds may be subdivided into two main divisions:

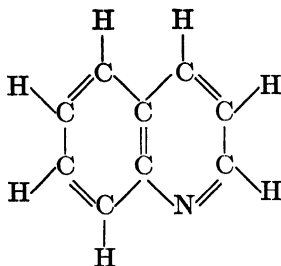
I. **Carbocyclic compounds**, containing a closed ring of carbon atoms such as benzene, for example,



II. **Heterocyclic compounds**, containing a closed ring which, in addition to carbon atoms, may contain one or more atoms of other elements, such as thiophene,

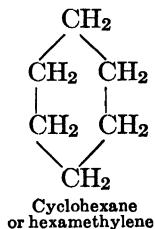
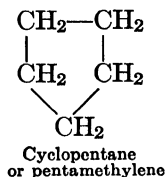
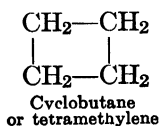


Combinations of carbocyclic and heterocyclic rings are also possible; for example, quinoline,



We have seen how the aliphatic series of compounds can be divided into typical groups, such as hydrocarbons, alkyl halides, alcohols, ethers, etc., and how the members of any one group show certain common characteristics which distinguish them from members of another group. Such typical divisions can also be made in the aromatic series, and here, to a certain extent, we find a series of compounds strictly analogous to those in the aliphatic series. Many of the type reactions which we shall consider in the following pages are those with which the student is already familiar.

We have seen how the hydrocarbons of the aliphatic series can be classified into paraffins,  $C_nH_{2n+2}$ , olefins,  $C_nH_{2n}$ , and acetylenes,  $C_nH_{2n-2}$ . A series of compounds isomeric with the olefins are the following:



Unlike the olefins, these compounds are not readily oxidized with potassium permanganate, and they form substitution rather than addition products. They cannot, therefore, be represented as compounds having double bonds. In fact, to a certain extent, they rather resemble the paraffins, despite the fact that they are isomeric with the olefins; hence they are spoken of as the **cycloparaffins**.

The cycloparaffins,  $(CH_2)_x$ , are really the connecting link joining the aliphatic compounds on the one hand, and the aromatic, on the other.



MARSTON TAYLOR BOGERT (1868- )

PROFESSOR OF ORGANIC CHEMISTRY, COLUMBIA UNIVERSITY, HAS DONE  
EXTENSIVE WORK IN SYNTHETIC ORGANIC CHEMISTRY AND HAS HAD MUCH TO  
DO IN BUILDING UP A SCHOOL OF ORGANIC CHEMISTRY IN AMERICA



## CHAPTER XXI

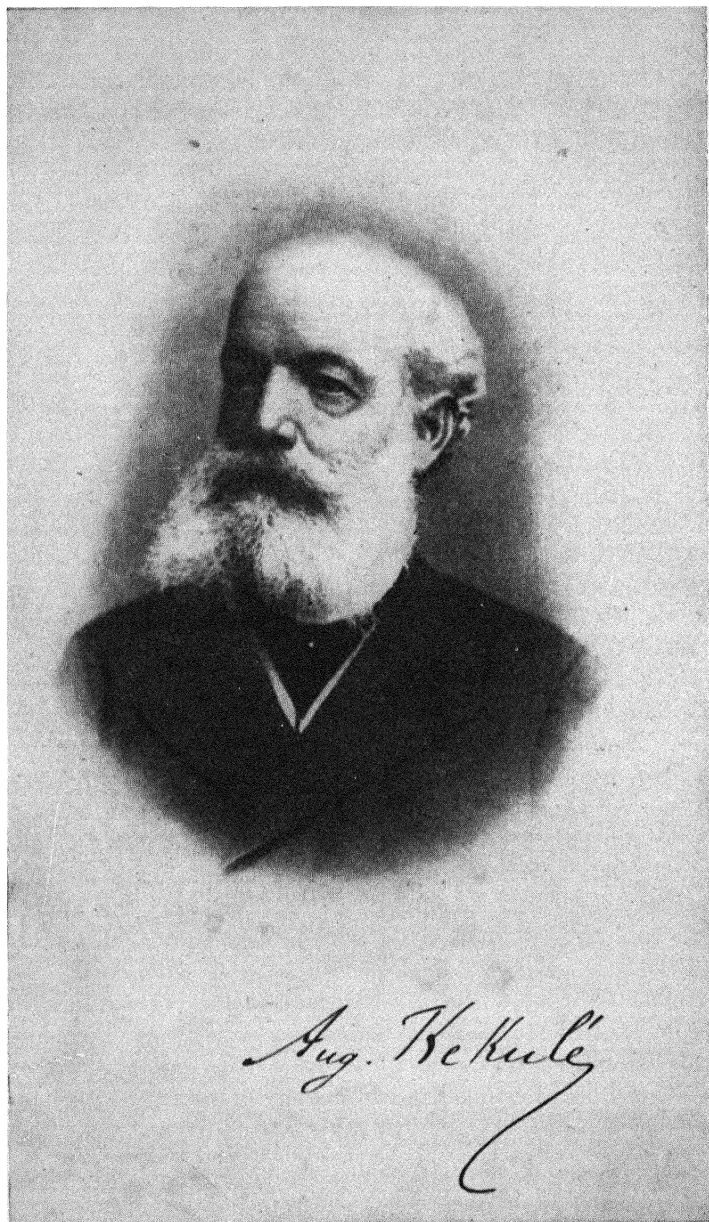
### CONSTITUTION OF BENZENE AND THE AROMATIC HYDROCARBONS

THE division of our carbon compounds into "aliphatic" and "aromatic" is no less arbitrary than the division of chemistry into "organic" and "inorganic." The word "aromatic" came into use because many of the naturally occurring substances had an agreeable aroma (such as oil of bitter almonds, oil of wintergreen, vanillin, gum benzoin, turpentine oil, etc.), and these were put into a class by themselves. But a classification based on odor is of little value. Many of the aliphatic compounds (such as the esters) have an agreeable odor, and many belonging to the aromatic series possess little, or no odor.

Aliphatic compounds (the compounds so far considered) have been represented as straight chain compounds while the aromatic compounds will be represented by closed chain or ring formulas.

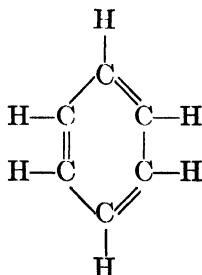
The aromatic compounds, as a whole, play a less important part in the chemical composition of living matter than do the aliphatic series. The proteins, fats, carbohydrates and phosphatides are largely of the aliphatic variety. On the other hand, many of the medicinals (drugs, antiseptics, etc.) come under the aromatic series. From the industrial standpoint, the vast group of synthetic dyes are largely recruited from the aromatic series.

As we have seen, the mother substance of the aliphatic series is methane,  $\text{CH}_4$ . The mother substance of the aromatic series, on the other hand, is **benzene**,  $\text{C}_6\text{H}_6$ . It will at once be seen that compared with methane, benzene is low in hydrogen; its structure ought, therefore, to show double or triple bonds. But its properties, however, are more those of a saturated hydrocarbon, and any constitution assigned to it similar in type to



FRIEDRICH AUGUST KEKULÉ (1829-1896)  
FIRST PROPOSED THE RING STRUCTURE FOR BENZENE AND ITS COMPOUNDS  
(P. 205).

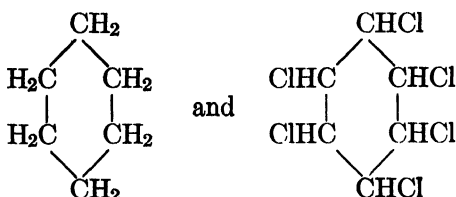
the one selected for ethylene or acetylene would grossly misrepresent the facts. This led Kekulé as far back as 1865 to propose a ring structure for benzene of the type:



and this formula is the one generally accepted to-day. It is no exaggeration to say that this benzene conception of Kekulé has proved of the utmost importance to the organic chemist, in giving him a tool with which to devise various possible chemical reactions.

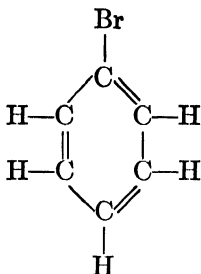
The structure of benzene, as suggested by Kekulé, is essentially that of a hexagon, containing six carbon and six hydrogen atoms. Any one hydrogen attached to a carbon atom is of equal importance to any other hydrogen attached to another carbon atom, and the carbon and hydrogen atoms all bear the same relationship to the molecule as a whole. There are, then, no preferences: any one atom in the molecule has exactly the same value as any other atom of the same element. The alternate double and single bonds satisfy the tetravalency of the carbon atom.

Kekulé's conception of the structure of the benzene molecule helps to explain many of the properties of benzene. According to this structure, the maximum number of hydrogen or chlorine atoms which can be added to benzene are 6, giving



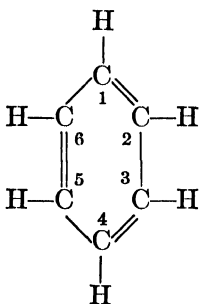
The addition of 6 hydrogen or 6 chlorine atoms implies the presence of three double bonds in the molecule.

If the benzene molecule is symmetrical and its carbon and hydrogen atoms are of equal value, then there can be but one, and no more than one, monosubstitution product, and the most extensive experimental work supports this view. For example, but one monobromobenzene,

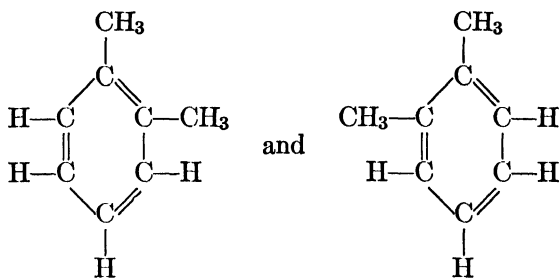


is known; it does not in the least matter to which carbon the bromine atom is attached.

On the other hand, Kekulé's benzene structure should allow for the possibility of three isomeric disubstitution products. If we number the carbon atoms as follows:

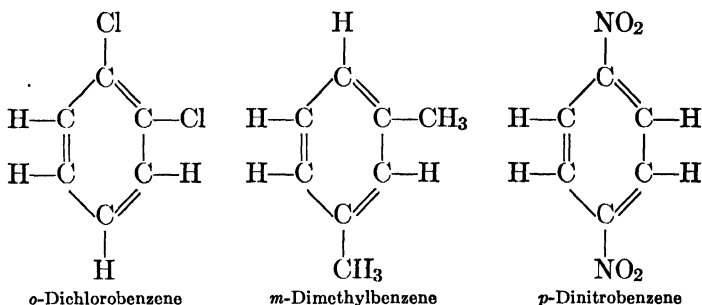


then we may have 1, 2, or 1, 6, or 2, 3 (or any adjacent pair) of hydrogen atoms replaced, giving an *ortho* (*o*-) compound; substitution in the 1, 3, or 2, 4, or 3, 5, or 1, 5 position will give a *meta* (*m*-) compound; and substitution in the 1, 4, or 2, 5, or 3, 6 position will yield a *para* (*p*-) compound.

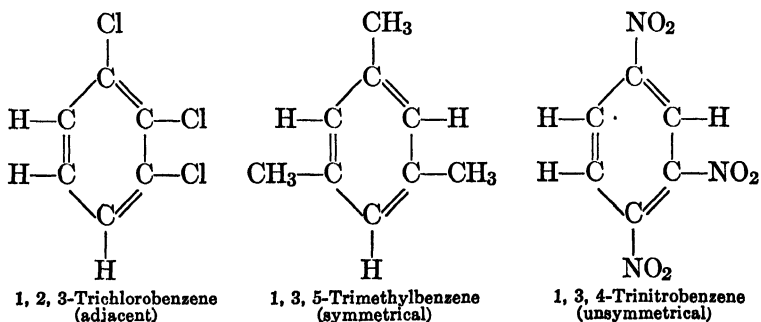


may be supposed at first sight to be different compounds, since in the one case the methyl groups are attached to two carbon atoms having a double bond in between, whereas in the other there is no double bond. But we must make the assumption that the double and single bonds are in continuous oscillation and not static.

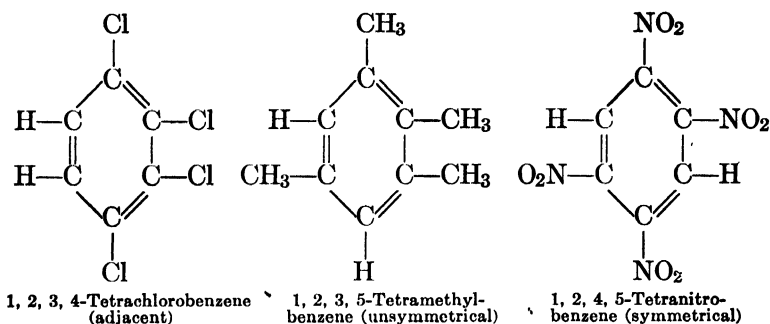
Examples of disubstitution products are



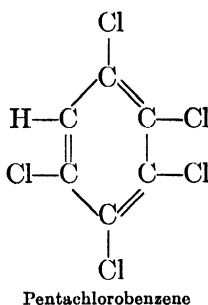
But three trisubstitution products are theoretically possible where the substituents are the same, and only three are actually known; e.g.,



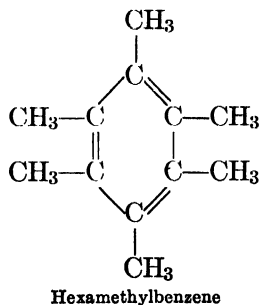
Where the tetrasubstitution products have like constituents, three isomers are possible: e.g.,



With five substituents, but one compound is possible: e.g.,

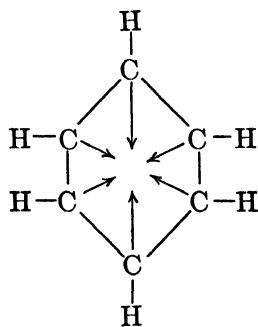
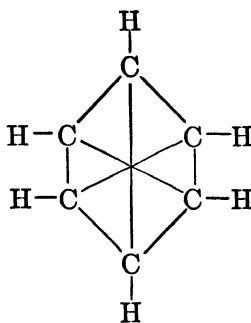


With six constituents but one compound is possible; e.g.,

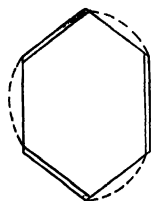


There were many objections in the past in representing the benzene molecule as having double bonds. The objections

are still raised by every beginner in the subject. His studies of the unsaturated hydrocarbons (p. 34) lead him to believe that a compound whose formula has one or more double bonds is "unsaturated," and by virtue of that fact, shows some very specific properties; but, as has already been pointed out, the properties of benzene are not really those of an unsaturated compound at all. For example, benzene, unlike the olefins, or other unsaturated aliphatic compounds, does not react with dilute potassium permanganate; it does not react with hydrogen bromide; and with bromine it forms substitution rather than addition compounds. This has led a number of investigators to suggest formulas for benzene which do not contain the usual type of double bonds, such as:


 Armstrong-Baeyer  
formula


Claus formula



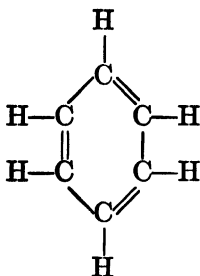
Thiele formula

and others. (For those interested, we may refer them to Richter's Organic Chemistry, Vol. II, p. 41 (1922)). However, Kekulé's formula is still preferred by the majority of organic chemists, because it explains many of the chemical characteristics of benzene and its derivatives.

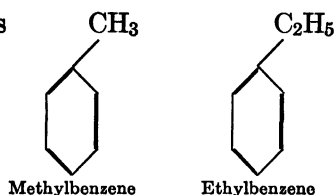
To simplify the writing of benzene and its derivatives we shall henceforth represent its structure as



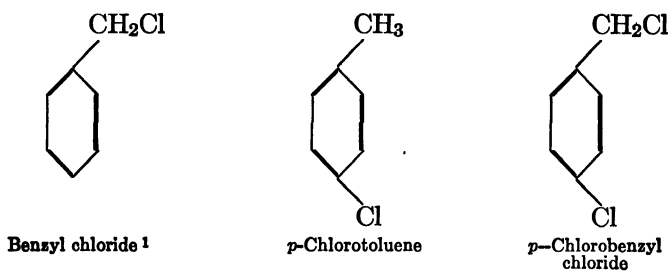
(Heavy lines indicate double bonds and light lines single bonds) bearing in mind that what is really meant is



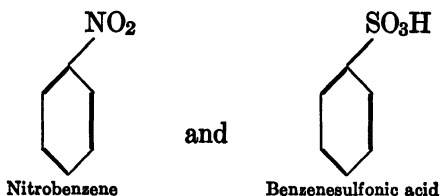
In the compounds



the  $\text{CH}_3$  and  $\text{C}_2\text{H}_5$  groups are spoken of as "side chains," the benzene residue being the "nucleus." Substitution may take place in the side chain, or in the residue, or in both, yielding various products; for example



Benzene differs from the paraffin hydrocarbons by the fact that whereas the latter are not acted upon by nitric or sulfuric acids, the former forms



<sup>1</sup> The  $\text{C}_6\text{H}_5\text{CH}_2$  (monovalent) group is known as the "benzyl" group.



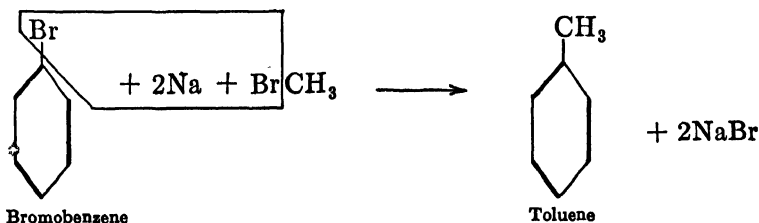
**Sources of Aromatic Hydrocarbons.**—The accompanying chart gives a list of the products obtained from the destructive distillation of coal and those of coal tar (among which we find the mother substances of the aromatic series of compounds, such as benzene, toluene, xylenes, naphthalene and anthracene).

("Benzene" is to be sharply distinguished from "benzine." The latter represents a mixture of hydrocarbons obtained from petroleum, whereas the former, as we have seen, is a definite chemical compound,  $C_6H_6$ . Benzene is also sometimes called "benzol," a word we owe to German chemists. This name has little to recommend it, and is confusing, since the ending "ol" is usually reserved for substances containing the OH group. In the industries, the expression "90 per cent benzol," signifies the fraction which distills below  $100^\circ C.$ ; it contains about 70 per cent of benzene.)

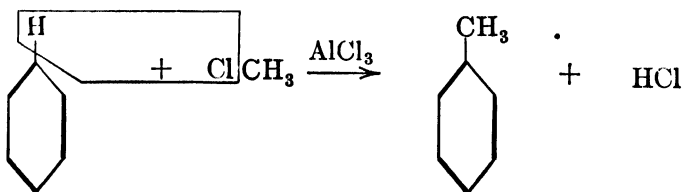
**Benzene and Some of its Homologues.**—Like the hydrocarbons of the aliphatic series, and like the various classes of organic substances, benzene is the starting point of a homologous series:

Benzene, $C_6H_6$	$C_6H_5$ group = phenyl (monovalent)
Toluene, $C_7H_8$	$C_7H_7$ group = tolyl (monovalent)
Xylenes, $C_8H_{10}$	$C_8H_9$ group = xylyl (monovalent)
Mesitylene, $C_9H_{12}$ etc.	The monovalent radicals of the aromatic hydrocarbons are known as the aryl radicals. (Cf. alkyl groups.)

**General Methods of Preparing Aromatic Hydrocarbons.**—The hydrocarbons may be prepared by the *Fittig* synthesis, analogous to the *Wurtz* reaction already studied (p. 21), which consists of treating a mixture of the appropriate halides with sodium; e.g.,

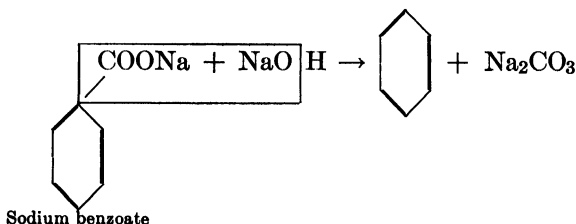


or by the *Friedel-Crafts* synthesis, in which the aromatic hydrocarbon and the appropriate halogen compound are made to react in the presence of aluminum chloride; e.g.,

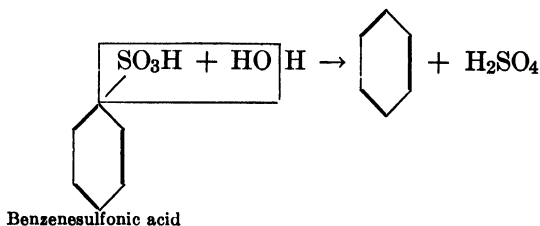


In this reaction  $\text{HX}$  is eliminated; the H atom must be linked to a carbon in a ring, while the X atom must be linked to a carbon not in a ring.

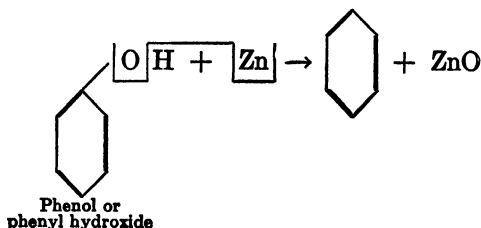
They may also be prepared by heating the salts of aromatic acids with soda lime—a reaction similar to one used in the preparation of the paraffins (p. 18); e.g.,



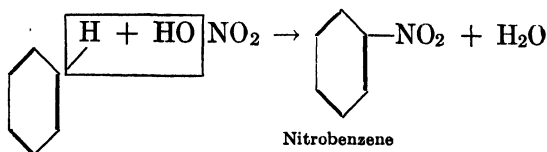
or, by the elimination of the  $\text{SO}_3\text{H}$  group from benzene compounds (by the use of steam, in the presence of acids); e.g.,



or, by distilling phenol with zinc dust; e.g.,

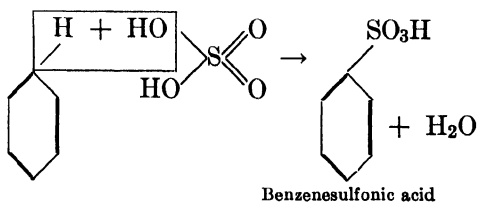


**General Reactions of Aromatic Hydrocarbons.**—Aromatic compounds react with nitric acid, forming nitro derivatives; e.g.,



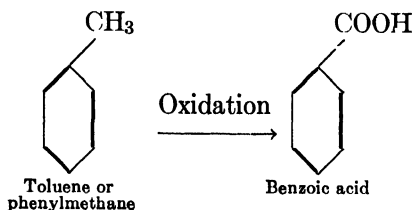
(This is known as **nitration**.)

They also react with sulfuric acid forming sulfonic acids; e.g.,



(This is known as **sulfonation**.)

The "side chain," whether  $\text{CH}_3$  or any other group, may be oxidized to the carboxyl group,  $\text{COOH}$ ; e.g.,

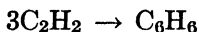


(These reactions—nitration, sulfonation and oxidation—bring out the essential differences of aromatic and aliphatic hydrocarbons.)

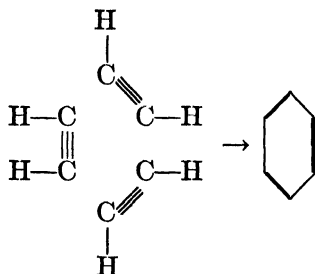
**Benzene**,  $\text{C}_6\text{H}_6$ , is the mother substance of the aromatic hydrocarbons. Commercially, it is obtained from coal tar. It is also present in California petroleum. It is a colorless liquid (b.p.  $80.4^\circ$ ), burning with a smoky flame (due to the high percentage of carbon), and when its vapor is mixed with air and ignited it is explosive. It is used as a solvent for fats, resins, etc., and in the manufacture of a large number of aromatic compounds; e.g., nitrobenzene, chlorobenzene, etc. Crude benzene (benzol) is used extensively in motor fuel. Benzene is a narcotic which

when swallowed or inhaled produces vertigo, delirium and convulsions.

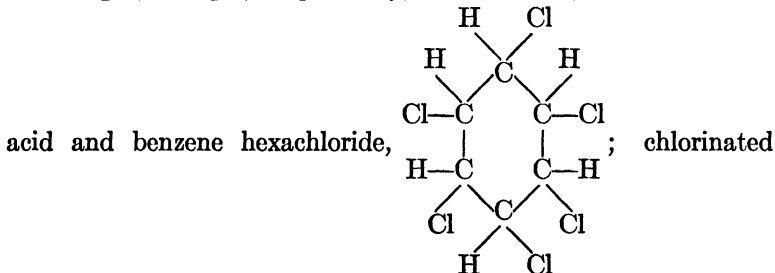
**Preparation.**—One method is to pass acetylene through a red hot tube:



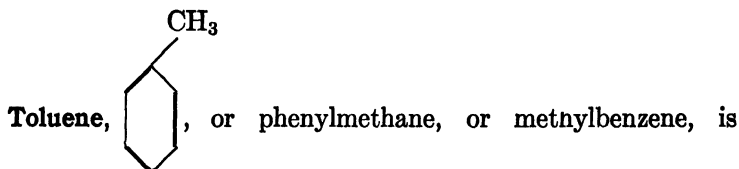
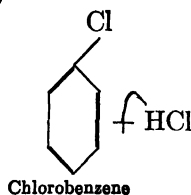
Here we have an example of how we can pass from an aliphatic to an aromatic compound—in this particular method, by “polymerization:”



With nitric and sulfuric acids, and with chlorine (long exposure to sunlight) we get, respectively, nitrobenzene, benzenesulfonic



in the presence of iron, aluminum iodine, etc. (catalysts or “carriers”), we get



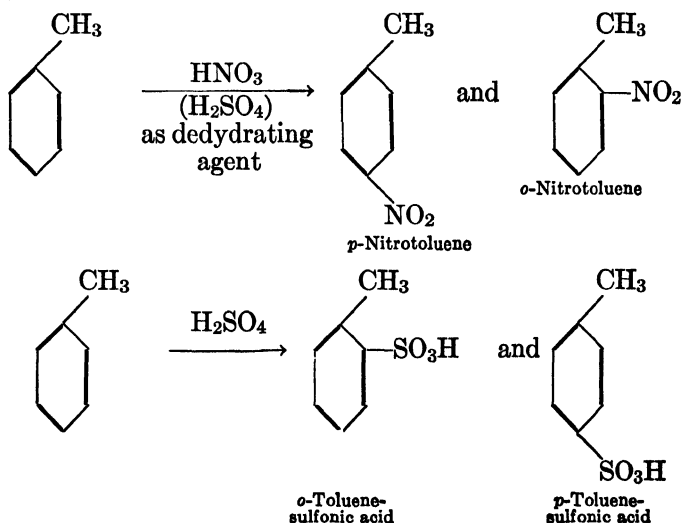
obtained from coal tar and also by the distillation of balsam of Peru and Tolu, b.p.  $111^{\circ}$ . ( $\text{C}_6\text{H}_5$ —monovalent is known as the “phenyl” group.) It may be prepared by the *Friedel-Craft* synthesis which has already been given (p. 212). Its properties are similar to those of benzene. When oxidized, it yields benzoic acid (p. 213).

**Rules for Substitution in the Benzene Ring.**—1. *If any one of the elements or groups, F, Cl, Br, I, R, OH, OR, CH<sub>2</sub>X, NH<sub>2</sub>, NHR or NR<sub>2</sub> (these contain single bonds) is present in the ring, an element or group that may next be introduced will take the p- and o- positions with respect to the first group.*

2. *If any one of the groups, NO<sub>2</sub>, SO<sub>3</sub>H, CHO, COOH, CO·R or CN (these contain double or triple bonds), is in the ring, an element or group that may next be introduced will take (largely) the m- position with respect to the first group.* (The amounts of m-, p-, and o- products formed depend very largely upon such factors as temperature, concentration of reacting substances, the type of dehydrating agent, and other experimental factors.)

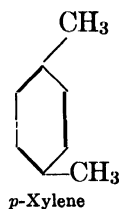
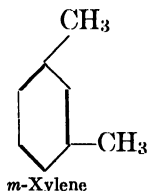
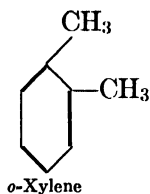
(It is essential before the student proceeds any further with the text that he thoroughly master these rules.)

An example of the application of these rules is immediately seen in the case of toluene. Toluene contains a methyl (R) group; hence, a second group will proceed simultaneously to the p- and o- positions; for example,

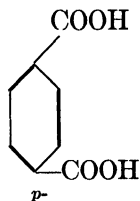
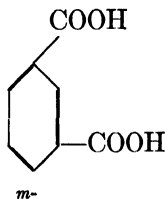
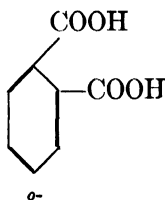



At low temperatures, the *o*- predominates, while at high temperatures the *p*-.

**Xylenes**, or dimethylbenzenes.—Since these are di-substitution products, three isomers are known:




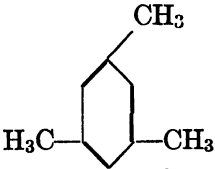
They are obtained from coal tar. On oxidation, the xylenes give the corresponding dibasic acids, indicating at the same time the position of the  $\text{CH}_3$  groups:

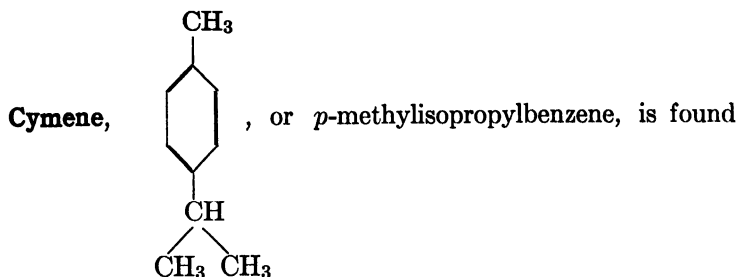


Ethyl benzene, , is an isomer of the xylenes, but is

easily distinguished from them by the fact that on oxidation it

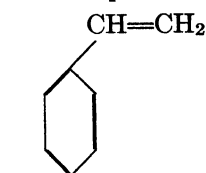
yields benzoic acid,  .

**Mesitylene**,  1, 3, 5 or symmetrical trimethylbenzene, is found in coal tar.

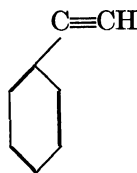


in oil of thyme, oil of caraway, oil of eucalyptus, etc.

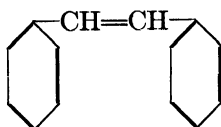
The number of hydrocarbons containing the benzene nucleus is large. Some are derived from coal tar, others are synthesized. A few of these compounds will be mentioned:



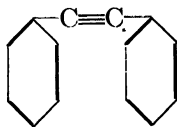
Phenylethylene  
or  
styrene



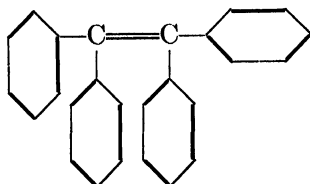
Phenylacetylene



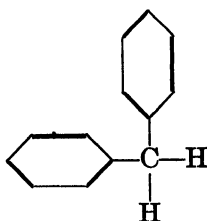
Symmetrical diphenyl-  
ethylene  
or  
stilbene



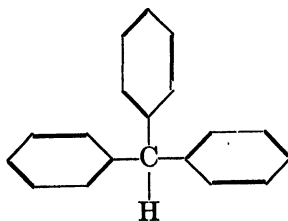
Diphenylacetylene  
or  
tolane



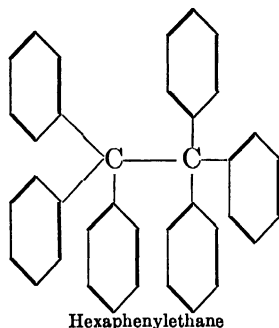
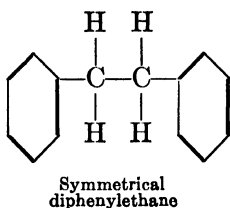
Tetraphenylethylene



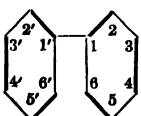
Diphenylmethane



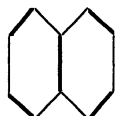
Triphenylmethane



(Gomberg, of the University of Michigan, in studying the action of zinc upon triphenylchloromethane, has obtained a substance, **triphenylmethyl**  $(\text{C}_6\text{H}_5)_3\text{C}\equiv\text{C}$ , in which one of the carbon atoms is apparently trivalent.  $(\text{C}_6\text{H}_5)_3\text{C}-\text{C}(\text{C}_6\text{H}_5)_3 \rightleftharpoons 2(\text{C}_6\text{H}_5)_3\text{C}$ . Since the structure of organic compounds is so intimately bound up with the view that the carbon atom is tetravalent, Gomberg's triphenylmethyl, with its trivalent carbon atom, opens up many new lines of research.)

**Diphenyl**, , or phenylbenzene, is made by the

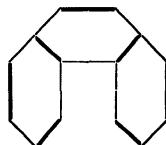
dehydrogenation of two mols. of benzene at an elevated temperature. Its high boiling point and its stability render this compound a very useful substitute for steam in boilers; it enables the apparatus to run at a higher temperature. Diphenyl, like benzene, may be chlorinated, nitrated, sulfonated, etc.



Naphthalene



Anthracene

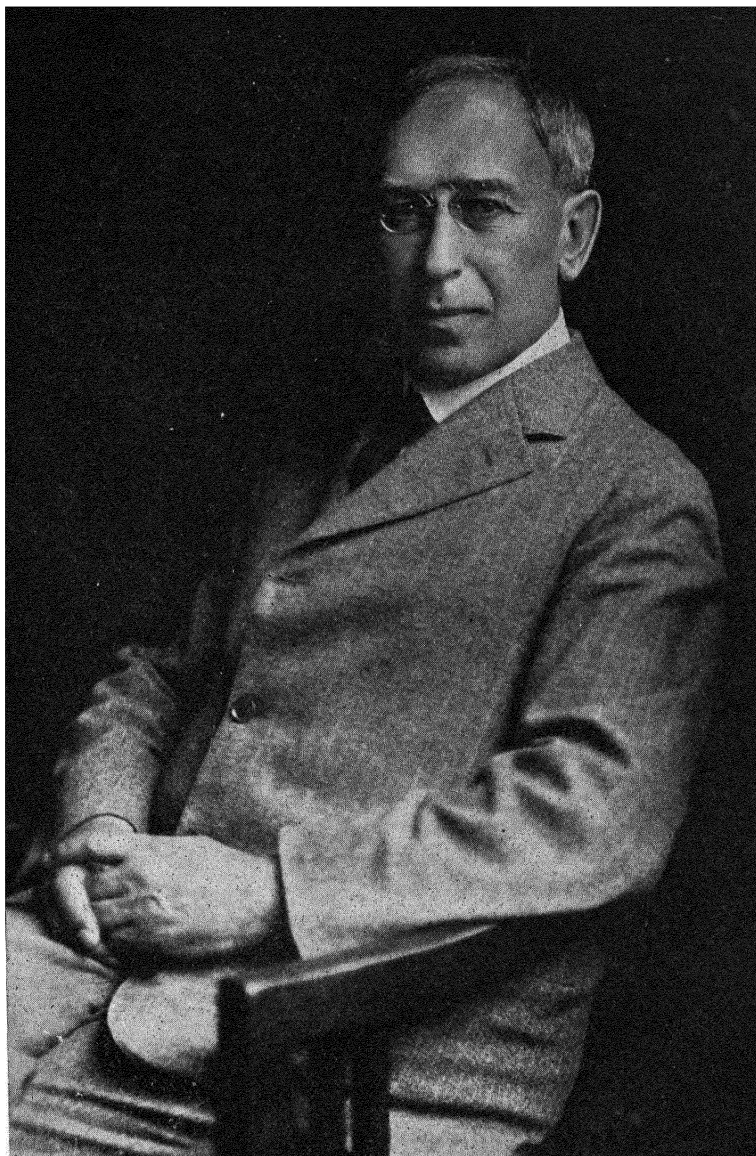


Phenanthrene

The last three compounds mentioned belong to the "condensed" or condensed cyclic series, and will be taken up in detail in Chapter XXVIII.

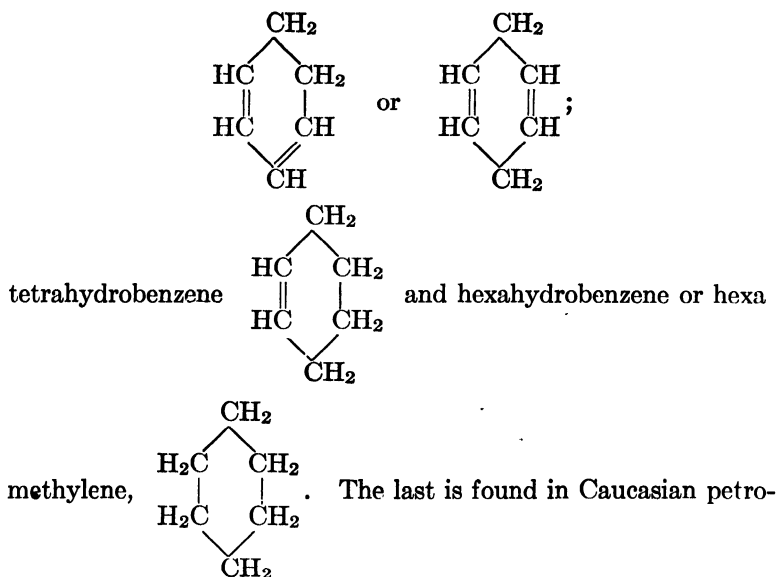
**Hydroaromatic hydrocarbons** are hydrogenated aromatic hydrocarbons; e.g., dihydrobenzenes:



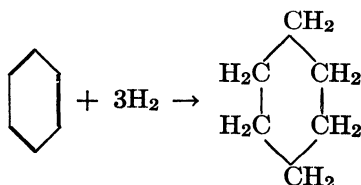


MOSES GOMBERG (1866- )

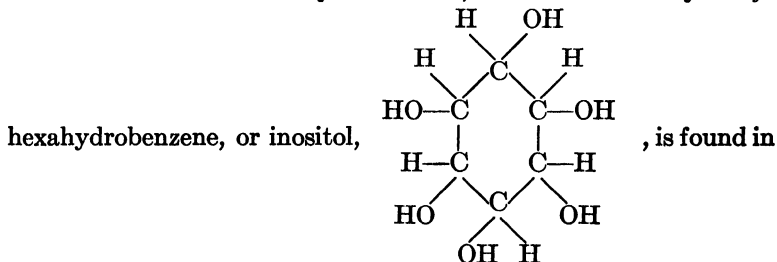
PROFESSOR OF CHEMISTRY AT THE UNIVERSITY OF MICHIGAN, IS ONE OF THE PIONEER WORKERS ON TRIVALENT CARBON AND FREE RADICALS (P. 218).



It and its homologues are known as the naphthenes. The hexamethylene may be prepared by the *Sabatier and Sendereu's* reaction (passing benzene vapor and hydrogen over finely divided nickel):



A derivative of hexahydrobenzene, known as hexahydroxy-



heart muscle and other animal organs, but is present in larger amounts in unripe beans and peas. The empirical formula for this compound is  $\text{C}_6\text{H}_{12}\text{O}_6$ , and it has often been called a cyclic sugar, though in reality it possesses none of the common properties

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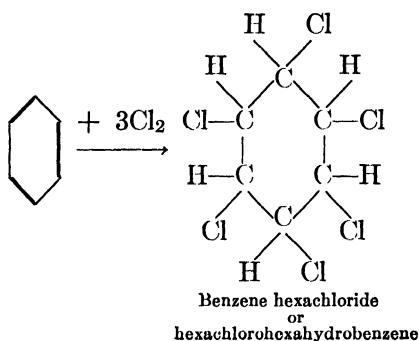
A two-reel motion-picture on "By-Product Coking" can be secured, free of charge, from The Koppers Company, Pittsburgh, Pa.

## CHAPTER XXII

### HALOGEN DERIVATIVES, SULFONIC ACIDS AND NITRO COMPOUNDS OF THE AROMATIC HYDROCARBONS

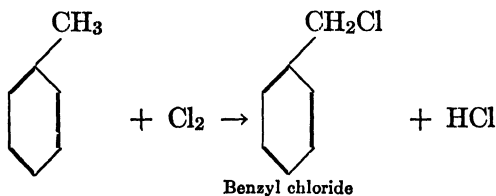
#### HALOGEN COMPOUNDS <sup>1</sup>

THE halogens may react in one of three ways with aromatic hydrocarbons: (1) they may form addition products; e.g.,



(This needs exposure to sunlight, but no carrier or catalyst.)

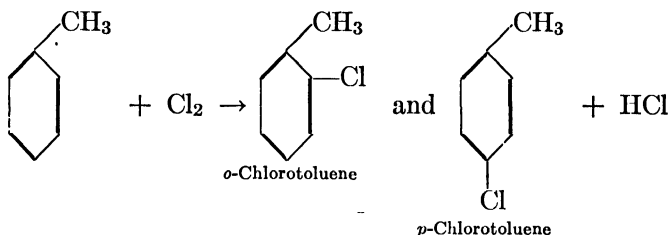
(2) Substitute in the side chain; e.g.,



<sup>1</sup> At this point the student is advised to review the chapter on aliphatic halogen compounds, p. 41.

(This is accomplished at the boiling temperature of toluene, in the presence of sunlight, or artificial light containing ultra-violet rays, but in the absence of a catalyst or halogen carrier.)

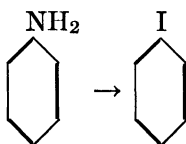
(3) The halogen may enter the ring; e.g.,



(This needs ordinary temperature, no sunlight and a carrier.)

The usual halogen "carriers" or catalysts, are  $\text{FeCl}_3$ ,  $\text{FeBr}_3$ ,  $\text{AlBr}_3$ , Fe, P, S, I, etc.

**Preparation.**—The halogen derivatives of the aromatic series may be prepared by direct halogenation with  $\text{Cl}_2$  or  $\text{Br}_2$ , as just described (iodine does not react), or by the conversion of the corresponding amino compound into the halogen derivative, where the halogen takes the place of  $\text{NH}_2$  : e.g.,




(See p. 243 for further details of the reaction.)

(Ethyl alcohol can be treated with hydrogen bromide, in the presence of sulfuric acid, to give  $\text{C}_2\text{H}_5\text{Br}$ , but when phenol,

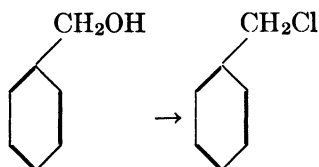


, is treated with hydrogen bromide, no analogous reaction

takes place. Again, when ethyl alcohol is acted upon by phosphorus pentachloride,  $\text{PCl}_5$ , we get  $\text{C}_2\text{H}_5\text{Cl}$ , but when phenol is

similarly treated, only a small yield of chlorobenzene,  is

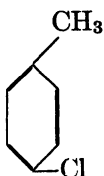
obtained. On the other hand benzyl alcohol is readily transformed into benzyl chloride by  $\text{PCl}_5$ :



Notice that here the side-chain reacts. (The side-chain, in fact, behaves like an aliphatic, rather than like an aromatic group.)

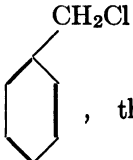
In the place of chlorine the following substances are sometimes used to introduce the element: thionyl chloride,  $\text{SOCl}_2$ ; chlorosulfonic acid,  $\text{ClSO}_3\text{H}$ ; sulfuryl chloride,  $\text{SO}_2\text{Cl}_2$ ; and sulfur mono- and sulfur dichloride,  $\text{SCl}$  and  $\text{SCl}_2$ .

**Properties.**—Where the X is attached to the ring, as in




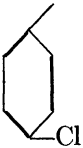



we get substances which may be colorless liquids or

solids, with an agreeable odor, and which are stable; where the X

is attached to the side-chain, as in , the compounds have

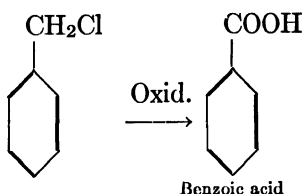
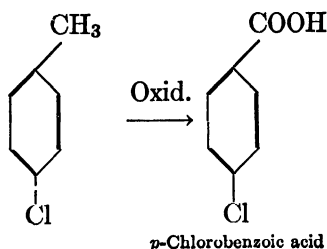
strong, disagreeable, pungent odors, are very reactive, and act as lachrymators. In general, they show the properties of the aliphatic halogen compounds of the type  $\text{RX}$ .

Some of the properties of the two types of halogen compounds may be summarized thus:

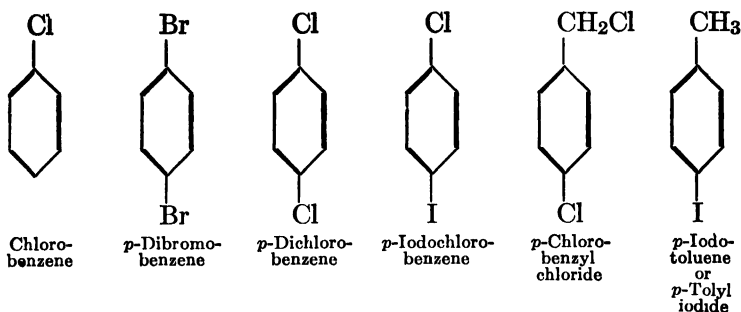
<b>Reagents</b>	$\text{CH}_2\text{Cl}$  Benzyl chloride	$\text{CH}_3$  p-chlorotoluene
<b>KOH</b>	$\text{CH}_2\text{OH}$  Benzyl alcohol	No reaction
<b>NH<sub>3</sub></b>	$\text{CH}_2\text{NH}_2$  Benzylamine	No reaction
<b>KCN</b>	$\text{CH}_2\text{CN}$  Benzyl cyanide	No reaction

from which it may be seen that where the halogen is attached to the nucleus, we get a relatively inactive compound; but where it is attached to the side-chain a very active compound, similar in its properties to the aliphatic halogen derivatives, is obtained. (The *Fittig* reaction exemplifies a typical reaction for the type where the halogen is attached to the nucleus.) The above reactions hold good only when carried out under atmospheric pressure. It has been noticed that at higher pressures reactions may be obtained even when the halogen is connected to the nucleus.

Whether the X is attached to the ring or to the side-chain, may be determined in some such way as the following:



Hundreds of halogen compounds are known; only a few will be mentioned:

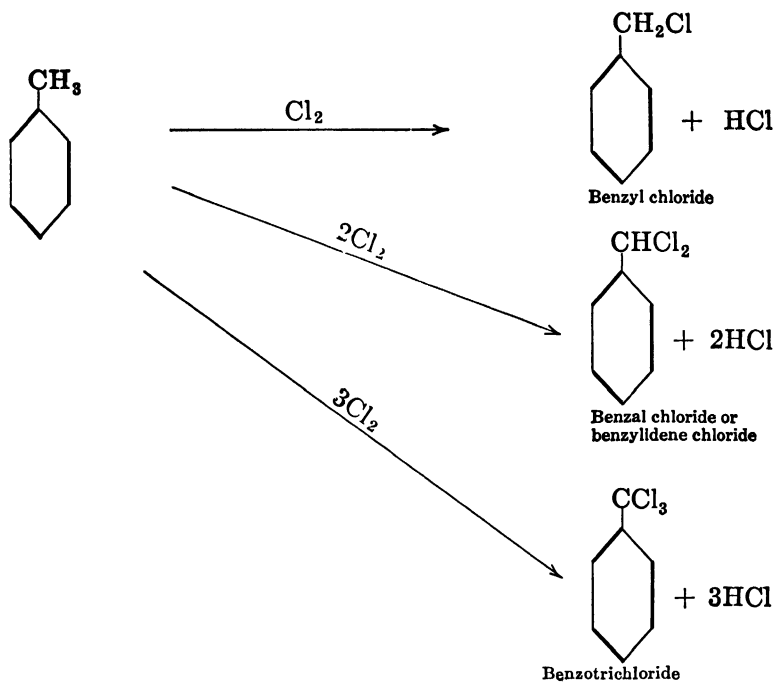


Chlorobenzene is manufactured by chlorinating benzene in presence of iron. It is used for the manufacture of dye intermediates.<sup>1</sup> *p*-Dichlorobenzene is used extensively to protect woolen goods from moths, and to protect the peach trees from the peach tree borer.

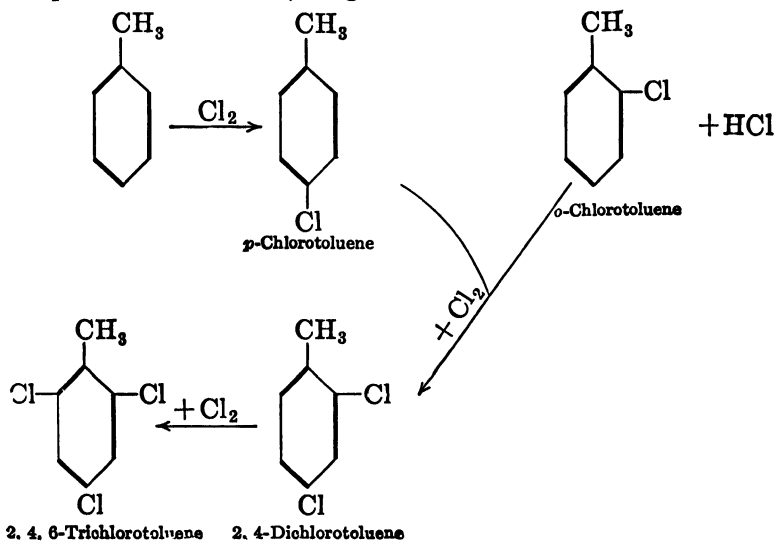
We may again refer to the preparation of these halogen compounds. Toluene, when acted upon by chlorine—in the presence of sunlight, in the absence of a “carrier,” in the absence of moisture, and at boiling temperature—gives the following products:

<sup>1</sup> A dye intermediate is an organic substance used in the manufacture of dyes.





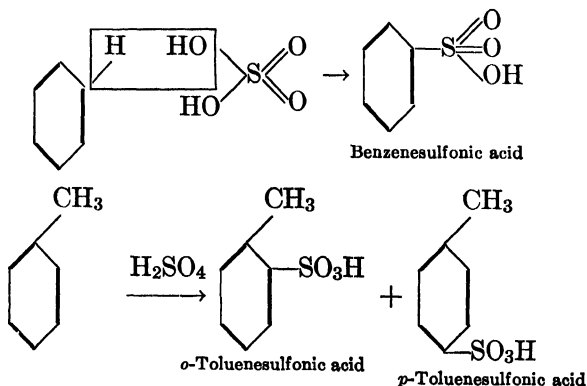
When, however, the chlorine and the toluene are made to react in the absence of sunlight and at room temperature, but in the presence of a carrier, we get:



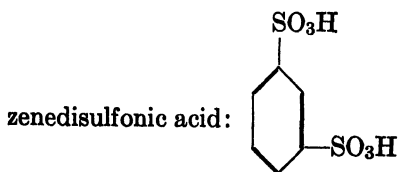
(A number of halogen derivatives of the aromatic series were used during the late war as **poison gases**. Some of these were benzyl bromide,  $\text{C}_6\text{H}_5\cdot\text{CH}_2\text{Br}$ , diphenylchloroarsine  $(\text{C}_6\text{H}_5)_2\text{As}\cdot\text{Cl}$ , phenylcarbylamine chloride,  $\text{C}_6\text{H}_5\cdot\text{N}=\text{C}=\text{Cl}_2$  and xylol bromide,  $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Br}$ , chloroacetophenone,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ . Since we are on the subject of war gases, we may include a few other compounds also used during the late war, although they really belong to the aliphatic series: bromoacetone,  $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{CH}_3$ ; bromoethyl methyl ketone,  $\text{CH}_3\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CH}_3$ ; chloroacetone,  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{CH}_3$ ; nitrotrichloromethane — or chloropierin —  $\text{CCl}_3\cdot\text{NO}_2$ ;  $\beta$ -dichlorodiethyl sulfide — mustard gas —  $(\text{C}_2\text{H}_4\text{Cl})_2\text{S}$ ; dimethyl sulfate,  $(\text{CH}_3)_2\text{SO}_4$ ; dichloromethyl ether,  $(\text{CH}_2\text{Cl})_2\text{O}$ ; phosgene,  $\text{COCl}_2$ ; trichloromethyl chloro-formate,  $\text{Cl}\cdot\text{COOCCl}_3$ , and hydrocyanic acid,  $\text{HCN}$ .)

### SULFONIC ACIDS

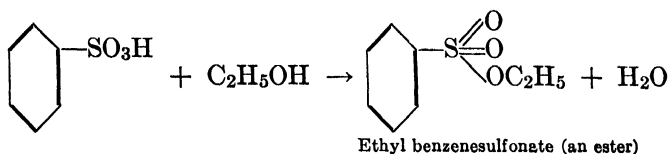
**Sulfonic acids** are a very important class of organic compounds since from them phenolic compounds (p. 250), naphthols (p. 297), etc., are prepared. They are generally prepared by the direct sulfonation of the hydrocarbon; e.g.,



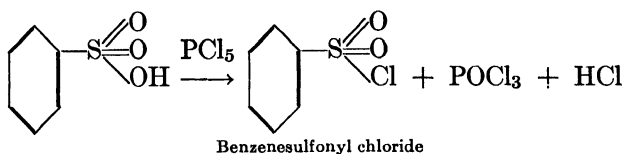
Benzenesulfonic acid when further sulfonated gives *m*-ben-



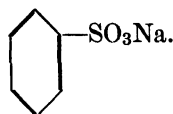
**Properties.** With alcohol, the sulfonic acids form esters; e.g.,



The corresponding chloride is obtained with  $\text{PCl}_5$ ; e.g.,

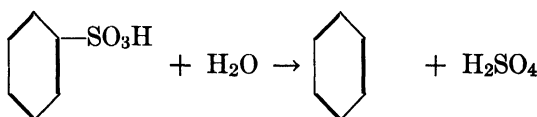


and with  $\text{NaOH}$  we form the sodium salt; e.g.,

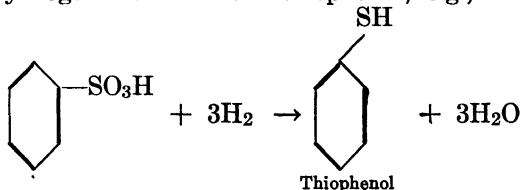


(Notice the analogous reactions of the  $\text{COOH}$  group and the  $\text{SO}_3\text{H}$  group above.)

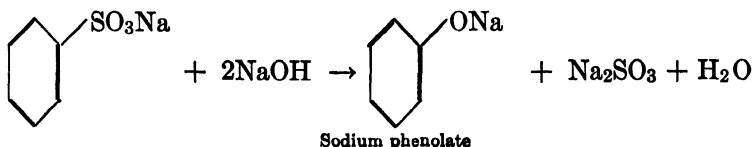
With steam under pressure, they are decomposed, yielding the hydrocarbon, e.g.,

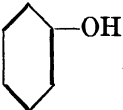


and with hydrogen are reduced to thiophenol; e.g.,



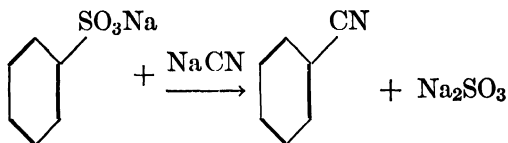
When fused with  $\text{NaOH}$ , the sulfonic acids yield the sodium salts of the phenols; e.g.,



from which the phenol, , can be obtained by treating the solution with  $\text{CO}_2$ . ( $\text{H}_2\text{CO}_3$ ).

(This is an extremely important commercial method used in the preparation of phenol and phenolic compounds. The sulfonic acid is first made from the hydrocarbon, then the former is fused with  $\text{NaOH}$ , and the resulting compound acidified.)

The sulfonic acids (salts) can be distilled with  $\text{NaCN}$  yielding the corresponding cyanides; e.g.,

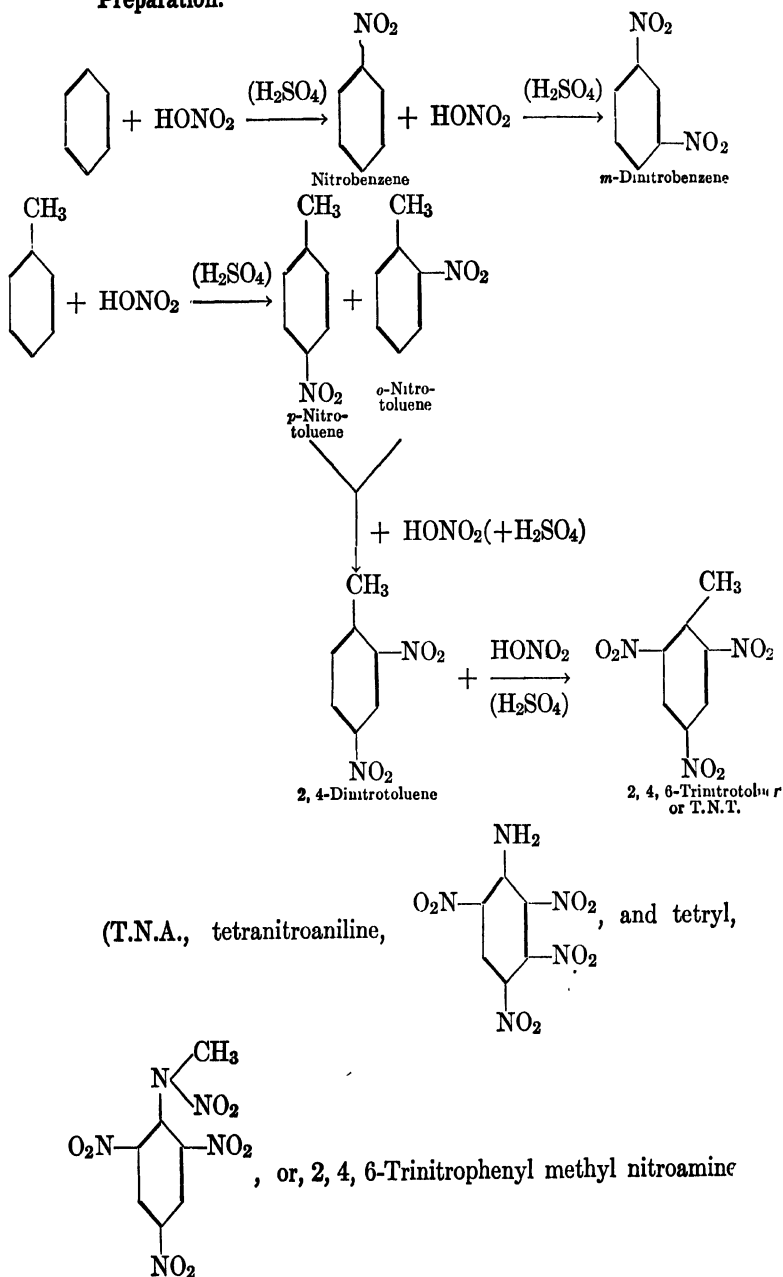


The free sulfonic acids are usually very soluble in water. In order to separate them from the excess of  $\text{H}_2\text{SO}_4$ , the  $\text{Pb}$ ,  $\text{Ca}$  or  $\text{Ba}$  salts are usually prepared. The  $\text{Pb}$ ,  $\text{Ba}$  and  $\text{Ca}$  sulfonates are soluble in water while the sulfates are insoluble. (For sulfonation, concentrated  $\text{H}_2\text{SO}_4$  at elevated temperature must be used. Very often it is necessary to resort to fuming  $\text{H}_2\text{SO}_4$ .)

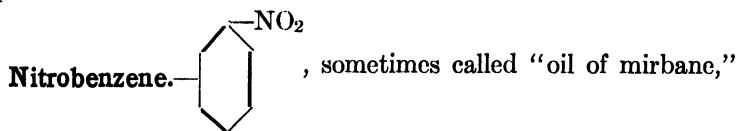
(Quite often organic compounds insoluble in water are sulfonated, converting them to water-soluble sulfonic acids. This is a procedure extensively used in the dye industry.)

### NITRO COMPOUNDS

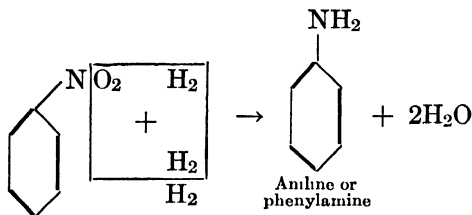
These are a very important class of organic compounds. They are generally prepared by direct nitration with  $\text{HNO}_3$ . In some instances the nitration proceeds readily, in others it does not. In some cases dilute nitric acid can be used (provided no oxidation takes place); in others the nitration will proceed only with concentrated or fuming nitric acid. Sometimes  $\text{NO}_2$  is used in place of nitric acid. In most cases the presence of sulfuric acid is necessary to absorb the water just as fast as it is formed in the reaction. Sometimes only fuming sulfuric acid will serve the purpose. In reality, a number of factors play their part in nitration—such as strength of nitrating acid ("mixed acid"— $\text{HNO}_3 + \text{H}_2\text{SO}_4$ ), amount of acid used, temperature of the reaction, length of time of nitration, agitation of the liquids, etc.

**Preparation.**

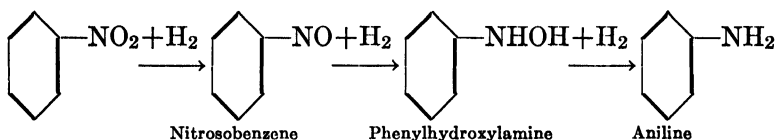
**Properties.**—The nitro compounds are usually pale yellowish liquids or solids, many of them being volatile with steam. Some of them—the higher nitro compounds, such as T.N.T.—are high explosives.



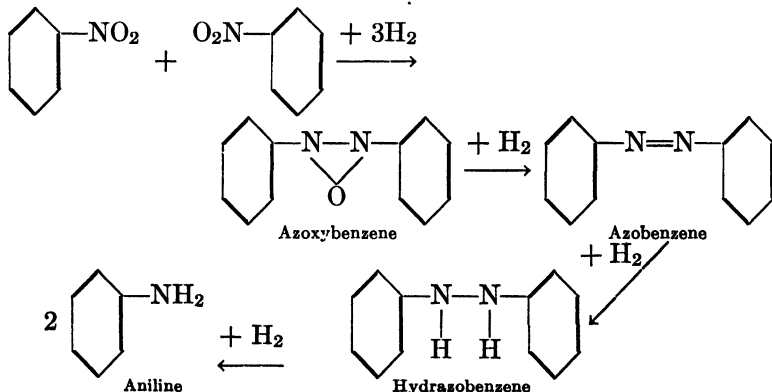
is a yellowish oil possessing the odor of bitter almonds, and is sometimes used in place of the latter in perfumes. It is also used in soaps, polishes and grease (due to its odor). It is manufactured from benzene on a very large scale for the purpose of preparing aniline, which is an important "dye intermediate,"

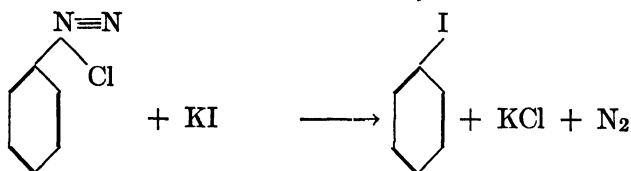
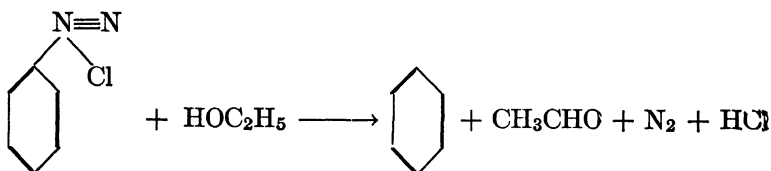
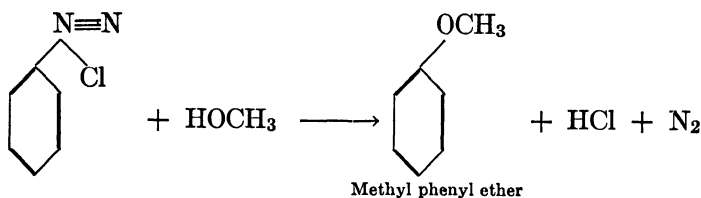
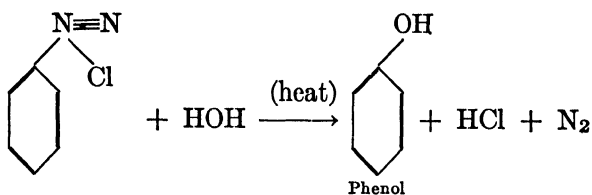


**Reduction products of nitro compounds under varying conditions:**

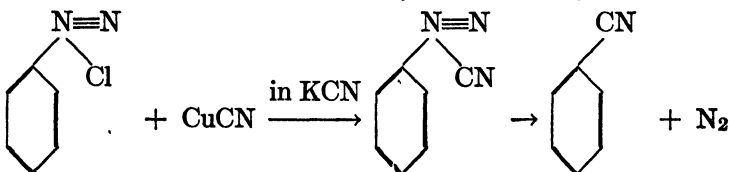
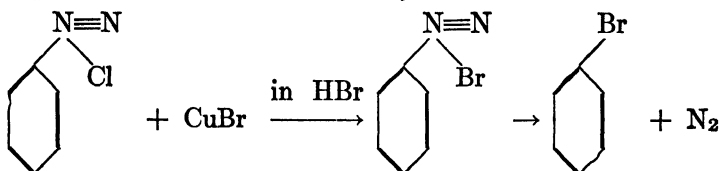
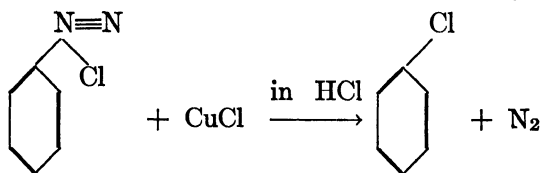


*Dimolecular Reduction Products:*

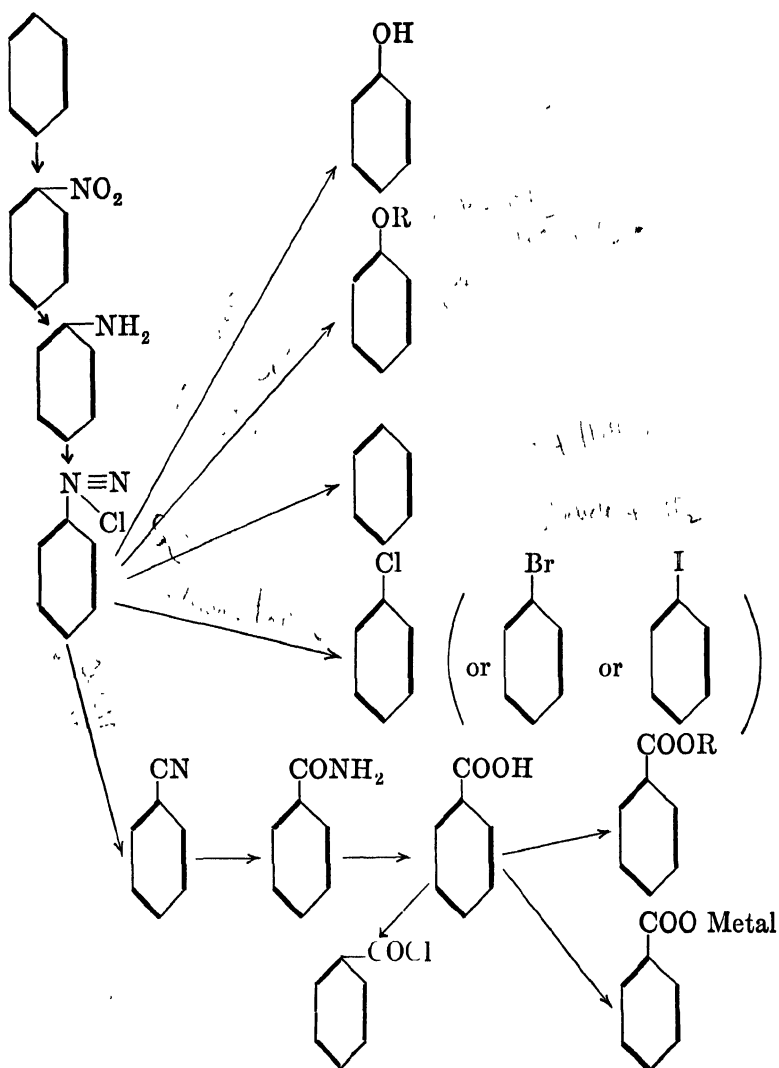




The following are known as the *Sandmeyer* reactions:



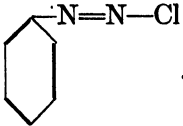
We may summarize these reactions to show the preparation of various types of aromatic compounds:



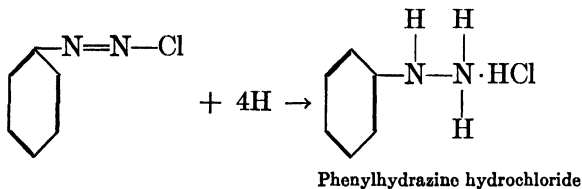
which gives an idea of the wide applicability which these diazonium compounds possess.

We must now proceed to reactions which are better explained



by the structure  . Upon partial reduction, the

following reaction takes place:

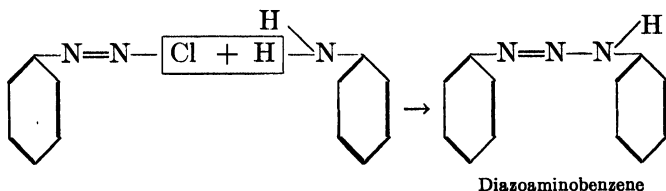


and the base, phenylhydrazine, , may be obtained

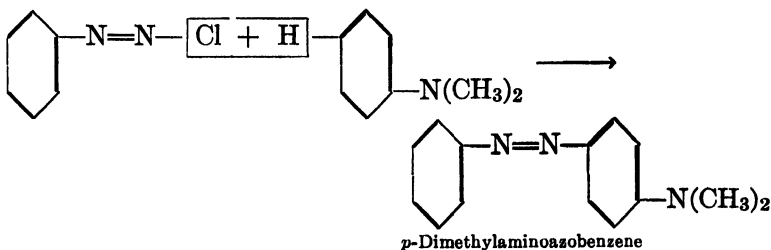
by the addition of NaOH. (Hydrazine is  $\text{H}_2\text{N}-\text{NH}_2$ .)

Phenylhydrazine, a poisonous liquid, has been used very extensively by Fischer and others in determining the structure of sugars. It is used in the identification of sugars (p. 169), in tests for aldehydes and ketones (p. 79), in the manufacture of antipyrine (p. 306) and various dyestuffs.

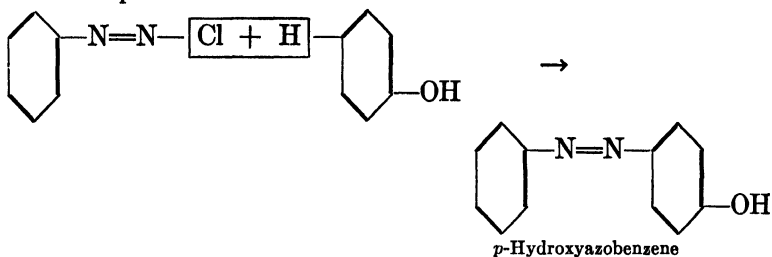
Diazobenzene chloride may be "coupled" with aniline (in neutral or weak acid solution) thus:



and with dimethylaniline:



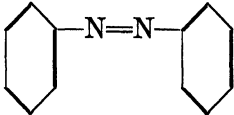
and with phenol:

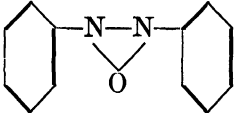


—reactions which are much better explained on the basis of a “diazo” rather than on a “diazonium” configuration.

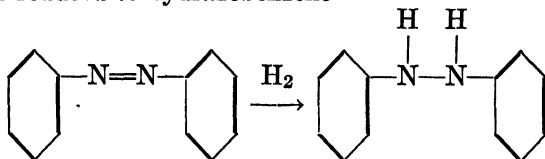
Reactions of the type just given are of great importance in the manufacture of azo dyes (p. 324).

The azo compounds are far more stable than the diazo compounds.

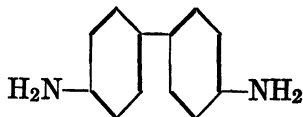
**Azobenzene**, , is prepared by distilling

azoxybenzene, , with iron filings; or by the

action of an alkaline solution of stannous chloride on nitrobenzene. It may be reduced to hydrazobenzene



which, when boiled with strong HCl undergoes an intramolecular rearrangement into *p,p'*-diaminobiphenyl, better known as **benzidine**:



which is an important dye intermediate. (Benzidine is also used in one of the tests to detect blood.)

## READING REFERENCES

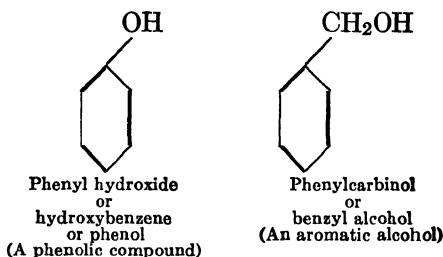
- GROGGINS—Aniline and Its Derivatives. (1924), chap. 1 (Discovery of Aniline Oil); chap. 4 (Acetanilide).
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## CHAPTER XXIV

### AROMATIC ALCOHOLS, PHENOLS AND ETHERS

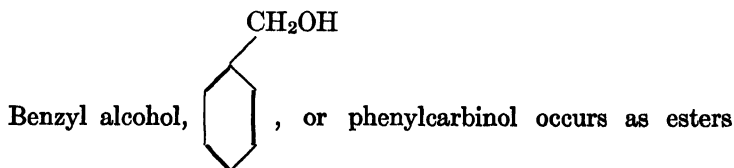
WE have already pointed out (p. 222) that in aromatic compounds substitution may occur either in the side-chain or in the nucleus, and that the products obtained when substitution takes place in the side-chain are quite different from those obtained when substitution takes place in the nucleus.

WE have seen, in the case of the amines, for example, how the  $\text{NH}_2$  group may be attached either to the nucleus or to the side-chain. This is equally true of the OH group. Where the OH is attached to the nucleus, it is known as a **phenolic** compound, and where it is attached to the side-chain it is an **aromatic alcohol**; e.g.,

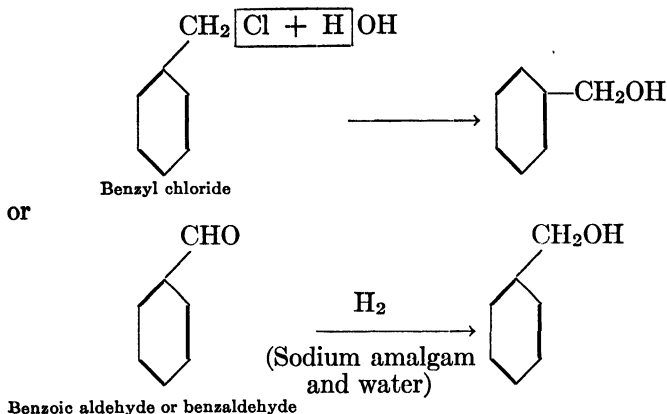


(In the aromatic alcohols, the OH group is attached to an alkyl residue, or side-chain; the properties of these compounds, therefore, are closely analogous to those of the aliphatic alcohols. See Chapter V.)

#### AROMATIC ALCOHOLS

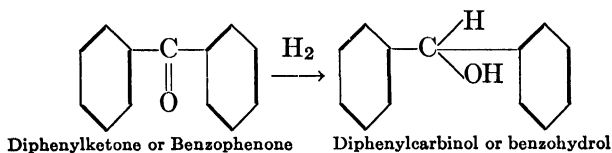


in balsam of Peru and Tolu, storax resin, in oils of flowers, etc. It may be obtained as follows:



It is used in perfumery, and in medicine as a local anesthetic.

Diphenylcarbinol, or benzohydrol, is a secondary alcohol, and may be prepared by reducing the corresponding ketone.



Cinnamyl alcohol,  $\text{C}_6\text{H}_5\text{CH=CH}\cdot\text{CH}_2\text{OH}$ , is present in

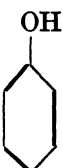
storax, and has an odor like that of hyacinth. It is used in perfumery.

Phenylethyl alcohol,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$ , is present in oil

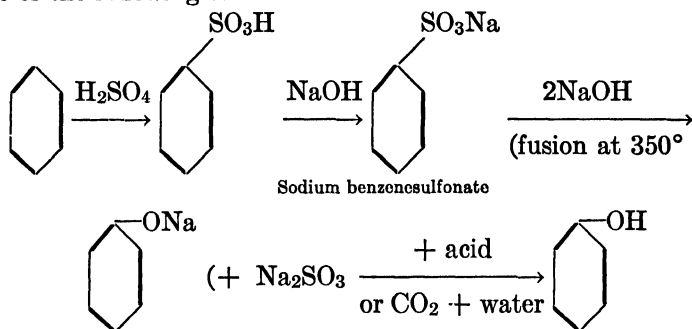
of rose and is used in perfumes.

## PHENOLS

The aromatic alcohols, like those of the aliphatic series, are neutral bodies, but when the OH enters the ring and we get a phenolic compound, then we obtain a very weak acid. The most important among these phenolic compounds is:

**Phenol**, , or phenyl hydroxide, or carbohic acid. It is

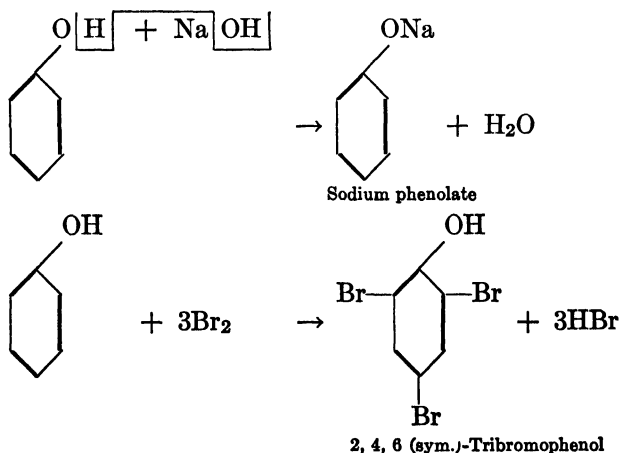
present in wood tar and coal tar (see chart facing p. 211), from which much of it is obtained. It is also manufactured by making use of the following series of reactions:

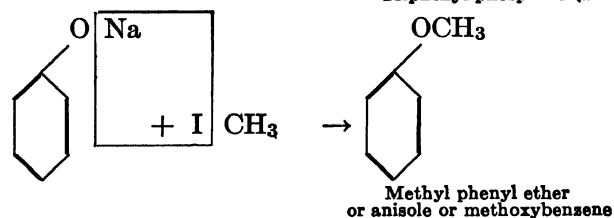
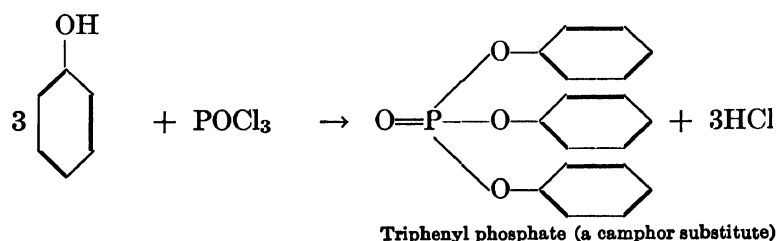
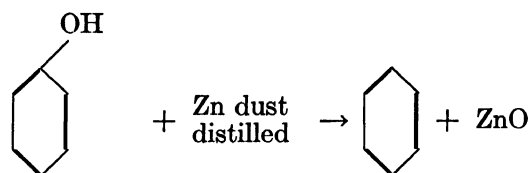
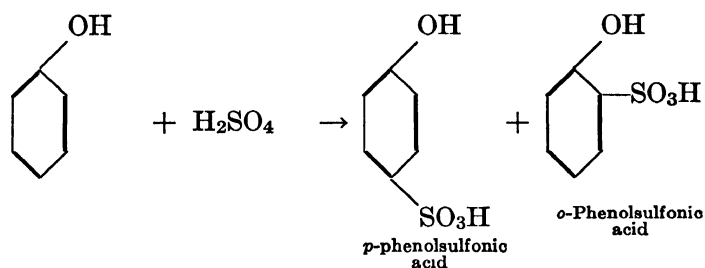
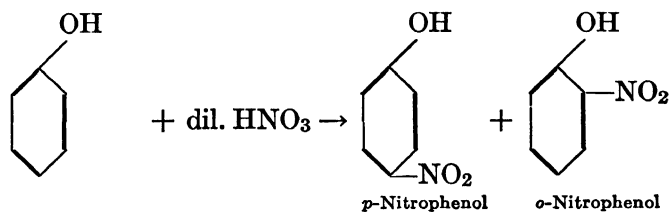
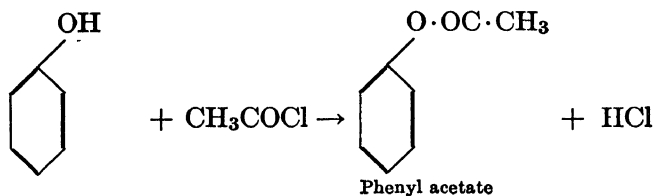


It may also be prepared by the diazo reaction (p. 243).

The most recent method for the preparation of phenol is by the hydrolysis of chlorobenzene with NaOH solution under high pressure.

**Properties.**—Phenol is a very weak acid but slightly dissociated (less so than carbonic acid). It is very corrosive and poisonous. Some of its general reactions may be illustrated by the following:





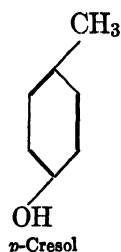
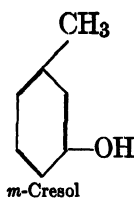
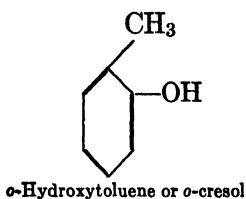
Phenol gives a violet coloration with ferric chloride. It is a colorless, crystalline substance which becomes liquid upon the addition of 15 per cent of water. It is a powerful antiseptic, disinfectant and germicide, and is used to a certain extent (in 3 per cent solutions) as a dressing for wounds, for disinfecting surgical instruments, rooms, etc.

Phenol is also used in the manufacture of explosives, dyes, developers, various medicinals, bakelite and other resins, etc.

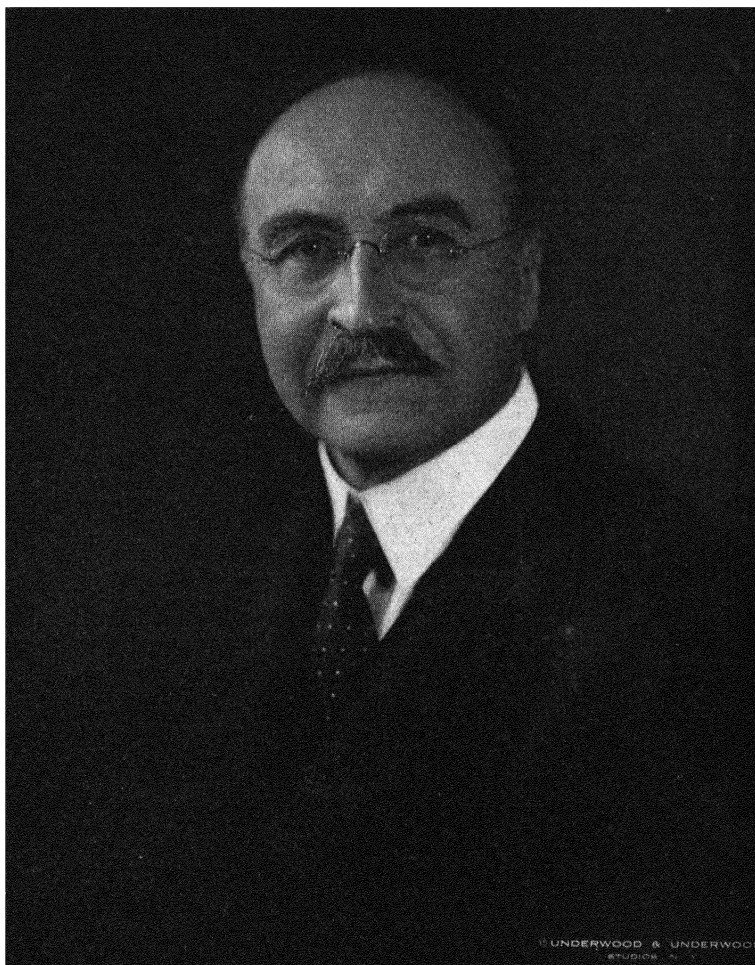
The resins, of which **bakelite** is an example, are sufficiently important to warrant a few words of description. Phenol combines with formaldehyde to produce a resinous material. These products—known as bakelite, etc.—vary in properties, for the particular type of resin obtained will depend upon the exact method employed in its preparation. Pure phenol and pure formaldehyde react very slowly, even when heated, but in the presence of catalytic agents, particularly bases—ammonia seems to be used in many cases—the action is accelerated. Where ammonia is used, it is believed that what first takes place is a reaction between the formaldehyde and the ammonia, forming hexamethylenetetramine (p. 80), and that the latter then combines with phenol, forming a resin, the chemical composition of which is not clear. This resin undergoes further changes when heated. It then becomes less fusible and less soluble. The raw bakelite, for example, is both soluble and fusible, but when heated becomes insoluble, infusible, very hard, strong and resistant. This bakelite is used in moulding materials, varnishes, enamels, lacquers, cements, pipe stems, cigar holders, handles, insulating substances, etc.

Recently glycerol and phenol have been made to combine to form a synthetic resin (called "acrolite") which has properties similar to the phenol-formaldehyde resin.

### Cresols.



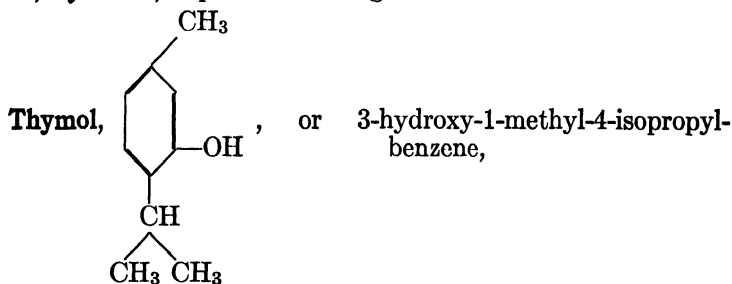




LEO HENDRIK BAEKELAND (1863- )

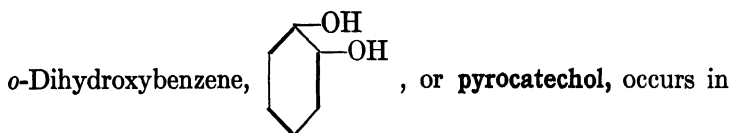
PRESIDENT OF THE AMERICAN CHEMICAL SOCIETY IN 1924 AND HONORARY PROFESSOR OF CHEMICAL ENGINEERING AT COLUMBIA UNIVERSITY, IS BEST KNOWN FOR HIS WORK ON "BAKELITE" (P. 252), SYNTHETIC PLASTICS IN GENERAL AND FOR "VELOX" (THE PHOTOGRAPHIC PAPER).

All three are present in coal tar and in wood tar, and all three act as antiseptics. They are known as "cresylic acid" or "tri-cresol." The properties of these cresols are, in general, similar to phenol. The cresols have greater germicidal power than phenol and are less poisonous. They are slightly soluble in water and are rendered more soluble by the addition of soap. Preparations such as lysol, creolin, phenoco, etc., contain cresols. Cresols are also used for the manufacture of synthetic resins, dyestuffs, explosives and organic chemicals.

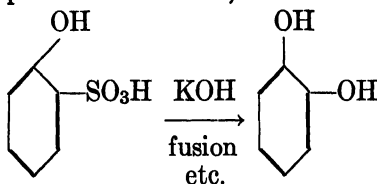


occurs in oil of thyme, mint, and other essential oils, and is an important antiseptic. It is very often used in the treatment of hookworm and to preserve urine. Diiododithymol (prepared from thymol and iodine) is known as "aristol" and has largely displaced iodoform as an antiseptic.

### Polyhydroxy phenols.

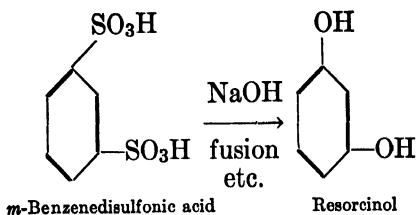


"catechu" resin and is prepared from resins by fusing them with KOH, or from *o*-phenolsulfonic acid;

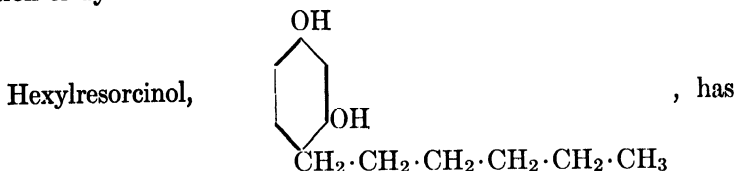


It is used in the manufacture of adrenaline and guaiacol.

Resorcinol, or *m*-dihydroxybenzene, or resorcin, is prepared thus:

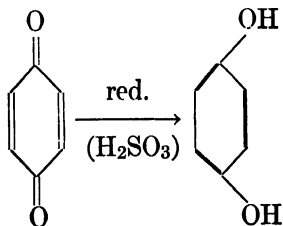


It is used as an antiseptic and an antipyretic, and in the preparation of dyestuffs.



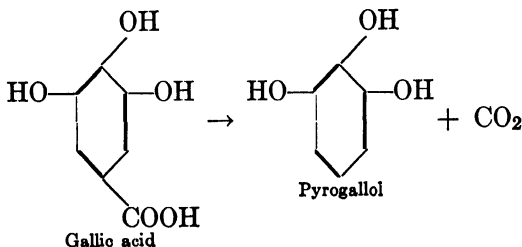
recently been introduced as an internal urinary antiseptic. It is one of the most powerful among organic germicides.

**Quinol**, or *p*-dihydroxybenzene, or hydroquinone, is prepared from *p*-benzoquinone (p. 265) by reduction:



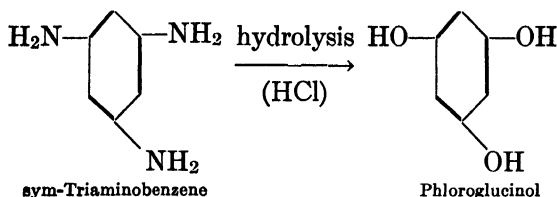
It is used as a photographic developer (that is, as a mild reducing agent, it being converted into benzoquinone).

Of the three trihydroxybenzenes, **pyrogallol** (or pyrogallic acid) is obtained by heating gallic acid:



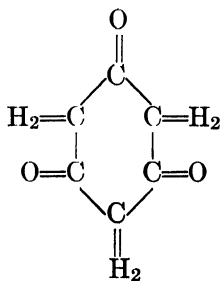
It is a strong reducing agent and absorbs oxygen in alkaline solution—a property used in estimating oxygen in gas mixtures. Pyrogallol is also used as a photographic developer and in the manufacture of dyestuffs.

**Phloroglucinol**, or sym. (1, 3, 5)-trihydroxybenzene, may be prepared from the corresponding triamino compound:



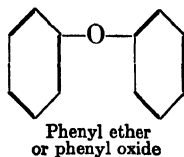
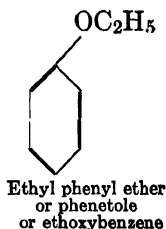
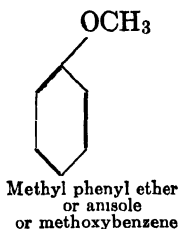
It occurs in the glucoside phloridzin and in different resins.

(The behavior of phloroglucinol towards reagents is worthy of discussion. That it is a trihydroxy compound is shown by the fact that it forms a triacetyl derivative with acetic anhydride. On the other hand, it forms a trioxime with hydroxylamine, indicating a ketonic structure—compare p. 135:

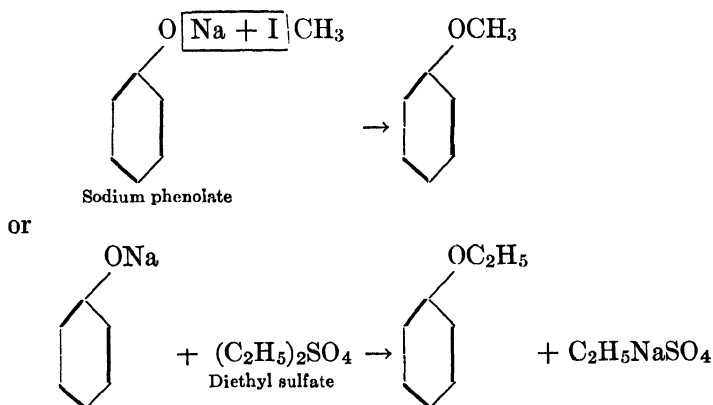


where, under certain conditions, the same compound may exist in two different forms, we have a case of **tautomerism**. This is to be distinguished from isomerism, where we have two different compounds having the same molecular formula.)

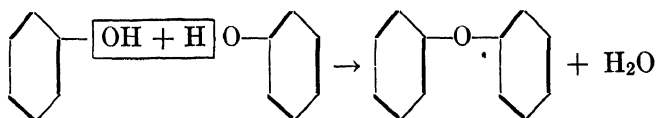
Phloroglucinol is used for the determination of furfural (p. 305)—a test based upon the production of a red color.

Ethers <sup>1</sup>

Ethers of the type of **anisole** and **phenetole** are produced thus:



The phenyl ether is prepared by heating phenol with zinc chloride:



It has a geranium-like odor.

These ethers are used in synthetic perfumes.

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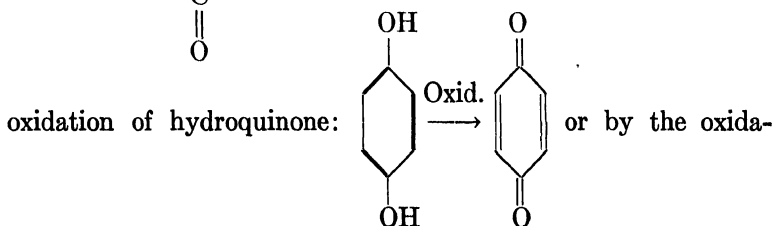
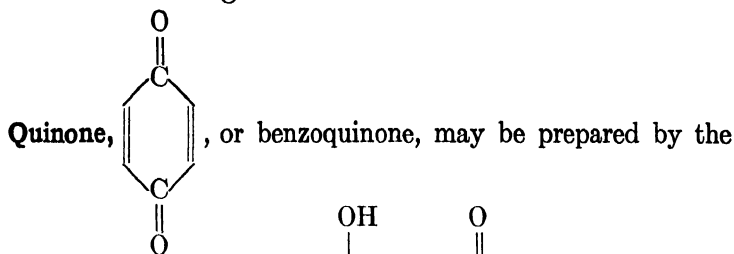
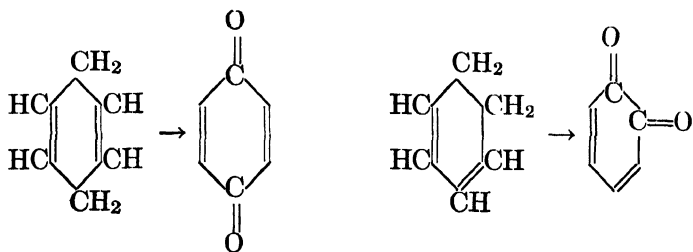
<sup>1</sup>The student is advised to review Chap. VI, p. 69.

- LEONARD—The Significance of Hexylresorcinol and Its Homologues in Relation to the Problem of Internal Antisepsis. *Science*, **62**, 408 (1925).
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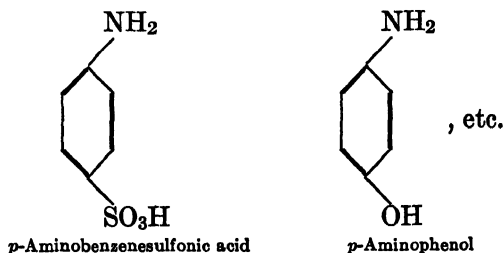
A motion picture on "The Story of Bakelite" can be secured from the Bakelite Corporation, 247 Park Ave., N. Y. City.

(When the 2CO groups are in the *p*-position with respect to one another, we get *p*-quinones, and when in the *o*-position, *o*-quinones. No *m*-quinones are known.)

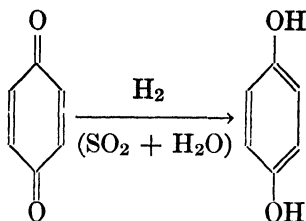
The quinones may be regarded as derivatives of dihydrobenzenes in which 2(CH<sub>2</sub>) groups are replaced by 2(CO) groups:



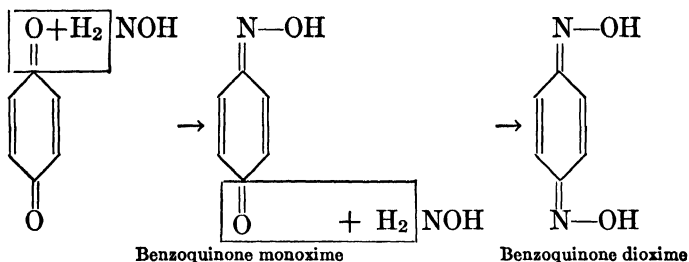
tion of aniline with  $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ ; or, by oxidizing amino and hydroxy compounds belonging to the *p*-series; such as



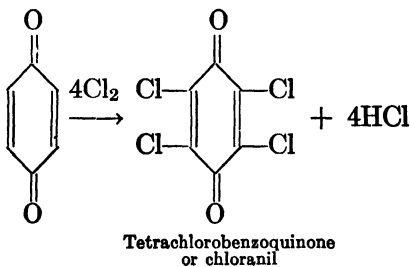
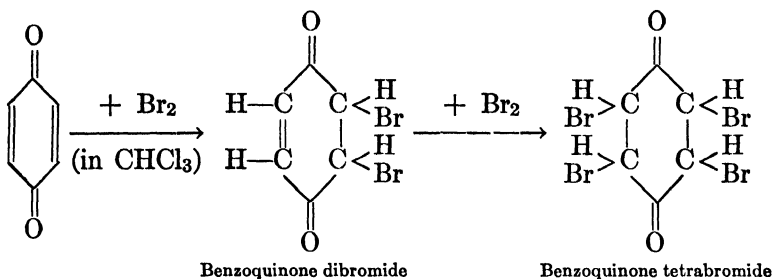
Benzoquinone is a yellow, crystalline solid, volatile with steam and possessing a pungent odor. It is reduced to hydroquinone;



Quinone forms mono- and di- oximes:



and halogen derivatives; e.g.,

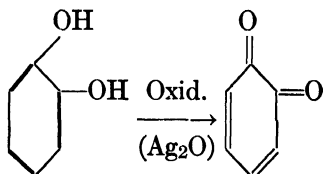


(The halogen compounds as shown above illustrate either addition products within the ring—a fact which suggests that these quinones are quite unlike benzene derivatives—or substitution products.)



When hydroquinone is heated with ferric chloride, quinhydrone precipitates. This quinhydrone may be looked upon as a molecular complex of one mol. of quinone and one of hydroquinone,  $C_6H_4(OH)_2 \cdot C_6H_4O_2$ . This quinhydrone is used very extensively in *pH* determinations.

***o*-Benzoquinone** is prepared from catechol by oxidation:



(The structure of quinones has been used to explain the chemistry of dyestuffs and the relationship between color and chemical structure. See p. 317.)

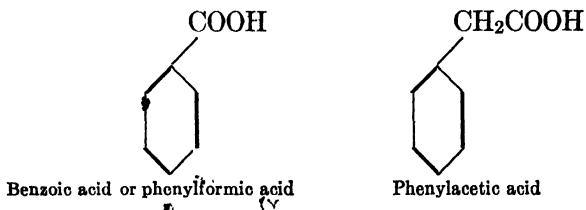
#### READING REFERENCES

- BOGERT—Recent Progress in Synthetic Perfumes. *Journal of Chemical Education*, **8**, 1311 (1931).  
SAMPEY—Addition Reactions of Conjugated Double Bonds. *Journal of Chemical Education*, **4**, 872 (1927).

## CHAPTER XXVI

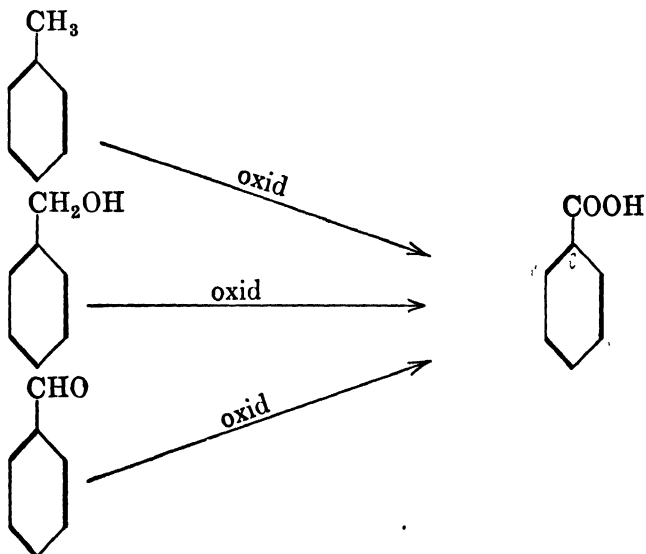
### AROMATIC ACIDS AND THEIR DERIVATIVES <sup>1</sup>

THE aromatic acids contain the COOH group attached directly to the ring or to the side-chain; e.g.,



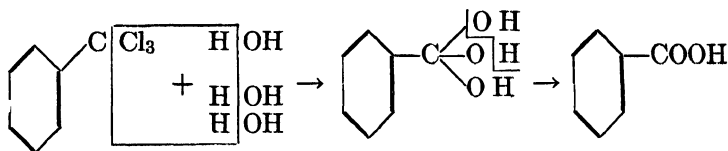
Many of the aromatic acids occur in nature (either in the free state or in the form of esters). We shall select benzoic acid as representative of the group.

**Benzoic acid** may be prepared by the oxidation of toluene, benzyl alcohol or benzaldehyde:

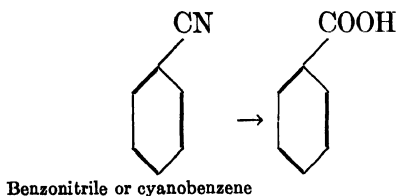


<sup>1</sup> The student should review Chaps. VIII, IX, XI, and XII.

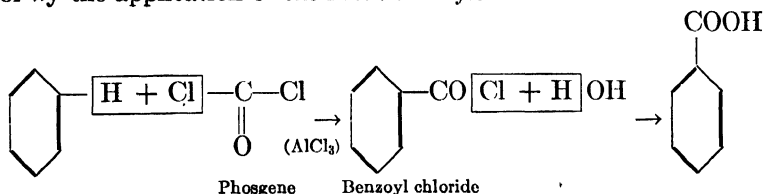
or by the hydrolysis of benzotrichloride:



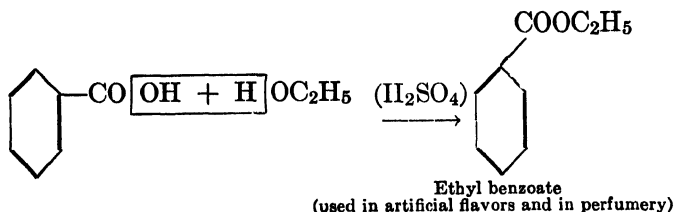
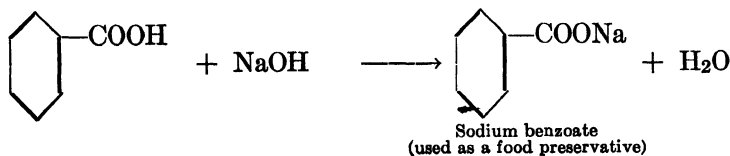
or by the hydrolysis of the corresponding cyanide:

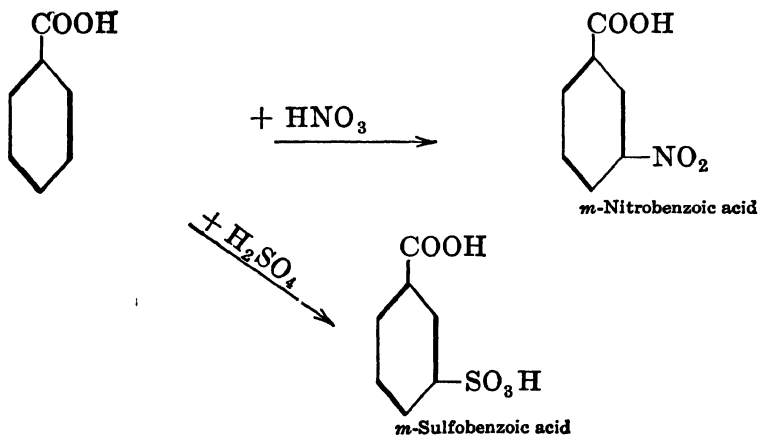
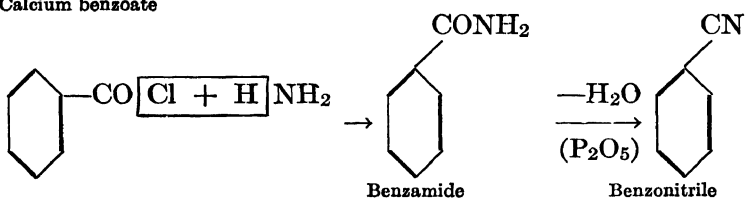
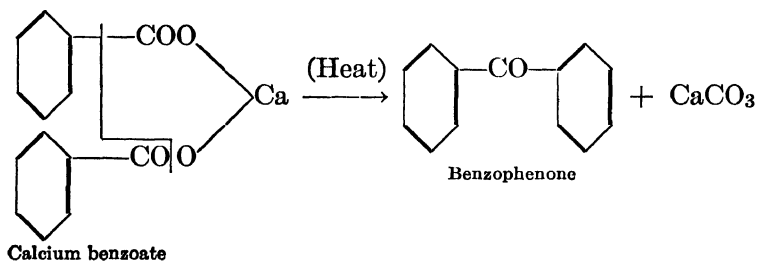
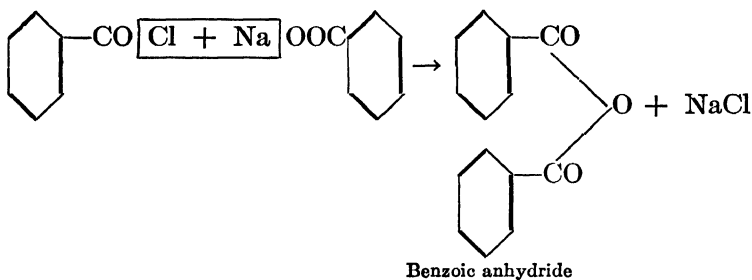
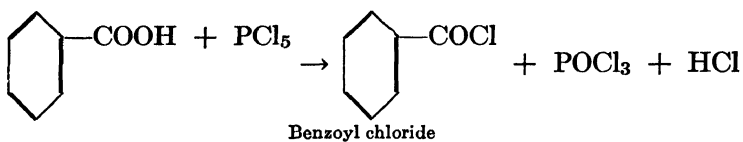


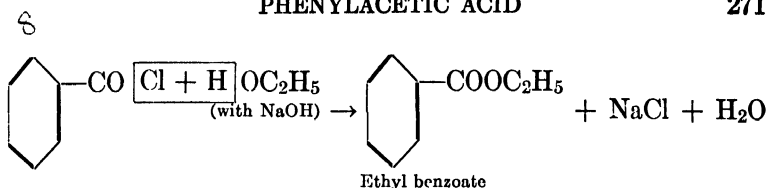
or by the application of the *Friedel-Crafts* reaction:



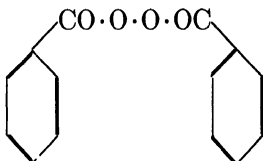
Benzoic acid occurs (as the free acid or as the ester) in gum benzoin, resins, balsams of Tolu and Peru, berries, etc. The free acid is generally purified by sublimation. Its properties are similar to those of compounds containing, on the one hand, a benzene nucleus, and on the other hand, a carboxyl group. Some of its reactions may be summarized as follows:







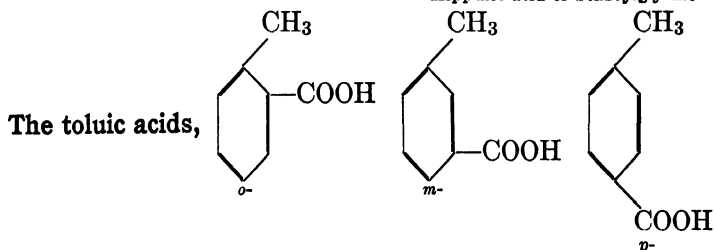
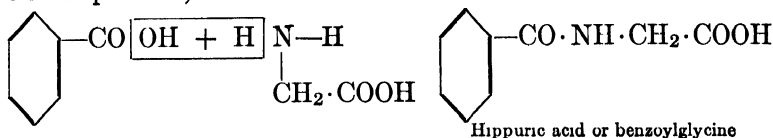
By the action of  $\text{Na}_2\text{O}_2$  on benzoyl chloride, benzoyl peroxide,




is formed. The compound is highly explosive. It is used for bleaching, for oxidation, and as a polymerization reagent.

Benzoic acid itself finds use in medicine as an antiseptic and also in the manufacture of dyes. Sodium, lithium and ammonium benzoates are used as internal antiseptics. Sodium benzoate is used as a food preservative. Benzyl benzoate is used in perfumery, as an anesthetic, and it possesses much of the pain relieving qualities of opium without any of the latter's toxic or habit-forming dangers.

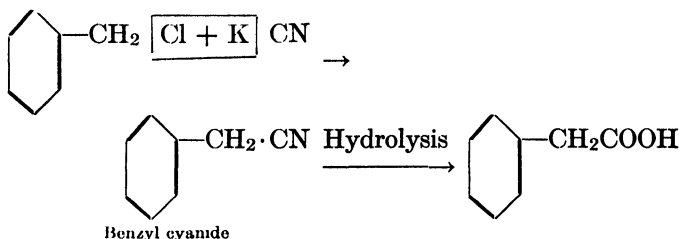
An interesting synthesis of hippuric acid in the body—by the kidneys—is brought about by the combination of benzoic acid (obtained from fruits, vegetables and, to some extent, proteins) and the amino acid, glycine, (obtained from the decomposition of proteins):




can be prepared by partial oxidation of the corresponding xylenes, or from the corresponding toluidines. (Diaz and *Sandmeyer* reactions.)

**Phenylacetic acid**, -CH<sub>2</sub>COOH, has its carboxyl group

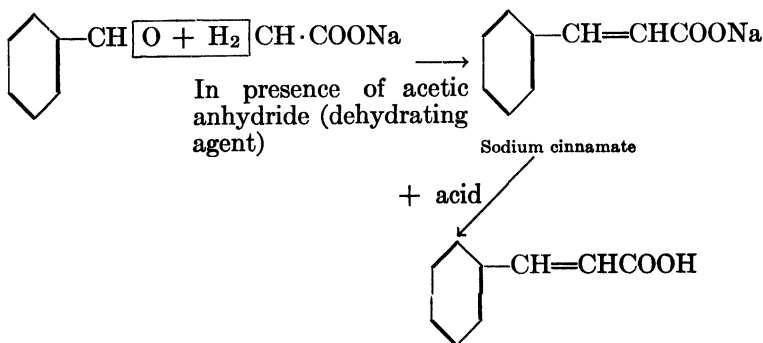
in the side-chain and is isomeric with the toluic acids. It may be prepared from benzyl chloride:




The acid and its esters are used in perfumery.

**Cinnamic acid**, -CH=CHCOOH, or  $\beta$ -phenylacrylic

acid, may be prepared by *Perkin's reaction*:

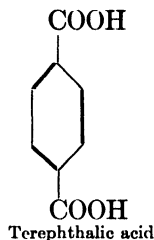
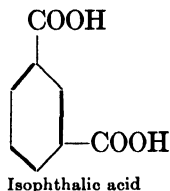
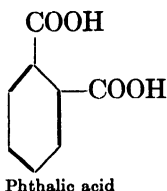


Esters of cinnamic acid and the acid itself are present in oil of cinnamon, resins, storax, balsams, gums, etc. The esters are used in flavoring materials and perfumery. The properties of cinnamic acid are those of a compound containing (a) a benzene nucleus, (b) a double bond structure, (c) a COOH group.

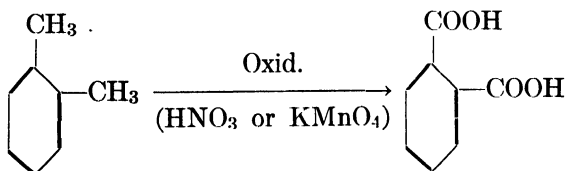
**Hydrocinnamic acid**, -CH<sub>2</sub>-CH<sub>2</sub>COOH, or  $\beta$ -phenyl-

propionic acid, is prepared from cinnamic acid by reduction (sodium amalgam and water).

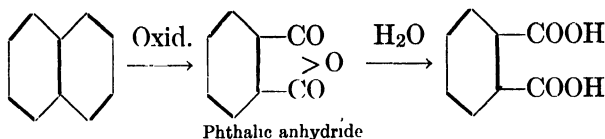
Of the phthalic acids,



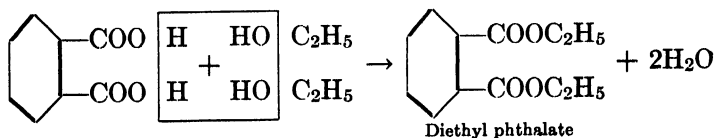
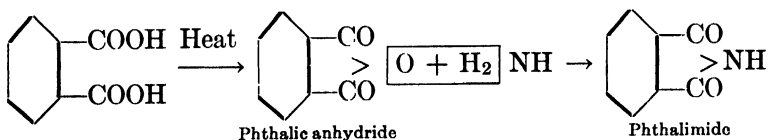
the first, or phthalic acid, is the most important; it is used in the preparation of over 200 compounds. It may be prepared by oxidizing *o*-xylene:



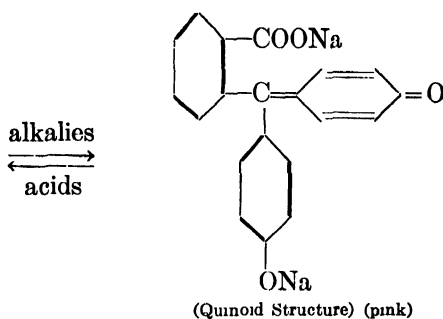
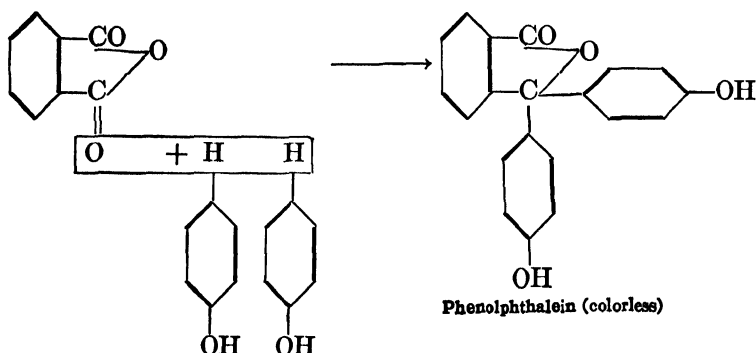
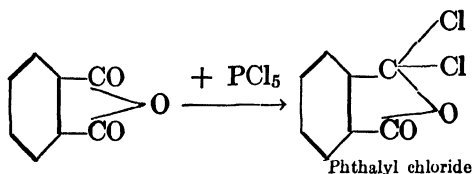
The commercial method is to pass the vapor of naphthalene and air over vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) (or other catalysts) at about 400°:



Some of the reactions of phthalic acid may be summarized:



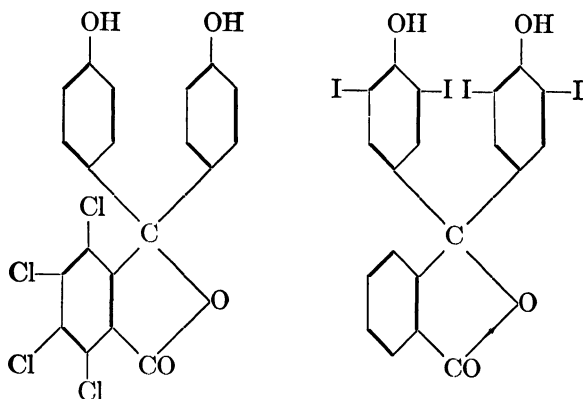
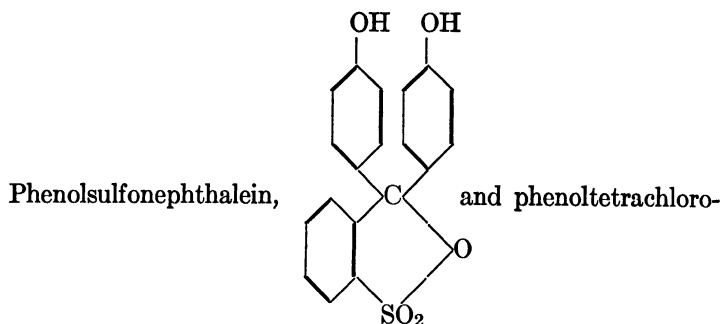
(The diethyl phthalate is a bitter substance and is used as a denaturant for ethyl alcohol.)



Phenolphthalein is one of the best-known indicators. It is also used as a purgative. Phthalic anhydride is used in the manufacture of anthraquinone (p. 302), and in the manufacture of several important dyes.

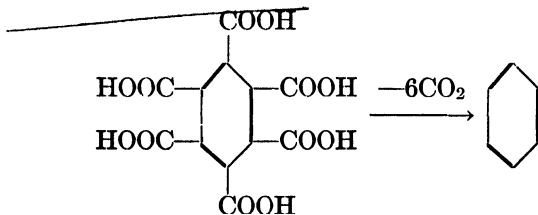
A considerable amount of phthalic anhydride is now being used in the manufacture of synthetic resins, such as glyptal, etc.





phthalein, and tetraiodophenolphthalein, are used to test the functional activities of the kidney and liver.

**Mellitic acid,** boxylic acid, may oxidation of graph- aluminum salt oc- mineral "honey stone." When heated with soda lime, the acid is converted into benzene: or benzene hexacar-  
be prepared by the  
ite with  $\text{HNO}_3$ . Its  
curs in nature as the



## READING REFERENCES

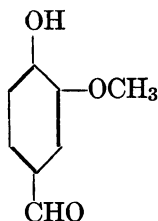
- SHERWIN—The Fate of Foreign Organic Compounds—Benzoic acid, etc.  
—in the Body. *Physiological Reviews*, **2**, 238 (1922).
- ANON.—Influence of Sodium Benzoate on Nutrition and Health of  
Man. (Agricultural Dept. Report 88.) Government Printing  
Office, Washington.

## CHAPTER XXVII

### ADDITIONAL AROMATIC COMPOUNDS CONTAINING MIXED GROUPS <sup>1</sup>

So far we have largely considered compounds containing single groups attached to the benzene ring, such as nitro compounds, sulfonic acids, phenols, aldehydes, etc.; and also, to some extent, a number of compounds containing dissimilar or mixed groups. In this chapter we shall consider additional compounds with unlike or mixed groups attached to the benzene ring. As thousands of such substances are known, only a few of the common and important ones can be mentioned.

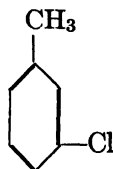
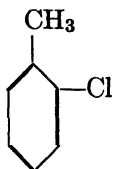
(Note to student: In studying the following compounds, the student should bear in mind that each group attached to the ring is responsible for certain characteristic reactions, and that the properties of the compound as a whole are, as a rule, the summation of properties exhibited by the individual groups present. For example, such a compound as



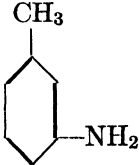
shows properties due (a) to the presence of the benzene ring, (b) to the OH group, (c) to the OCH<sub>3</sub> group and (d) to the CHO group.)

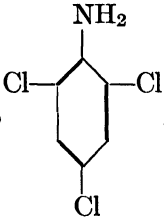
<sup>1</sup> The student is advised at this point to review the rules for substitution in the benzene ring (p. 215).

**Chlorotoluenes**, or tolyl chlorides.—Three isomers are known:

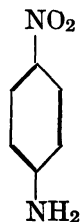
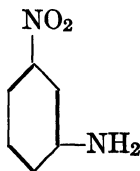
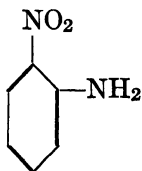


A mixture of the first two (*o*- and *p*-) is obtained when toluene is chlorinated (in presence of a halogen carrier). Direct chlorination of toluene does not yield the third, or *m*- variety; but we

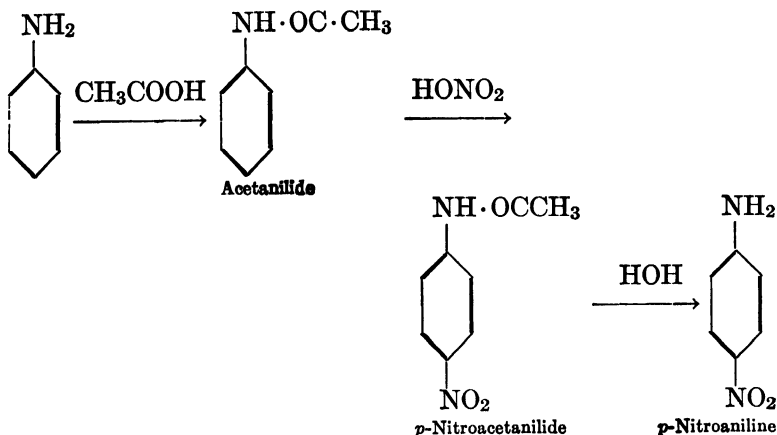
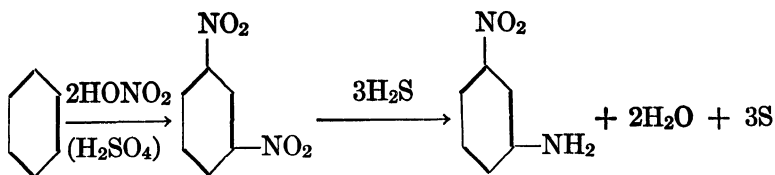
may start with *m*-toluidine, , diazotize it, and apply the *Sandmeyer* reaction (p. 243).

Three isomeric **chloroanilines** are known. When aniline is treated with chlorine, sym.-trichloroaniline, , is obtained.

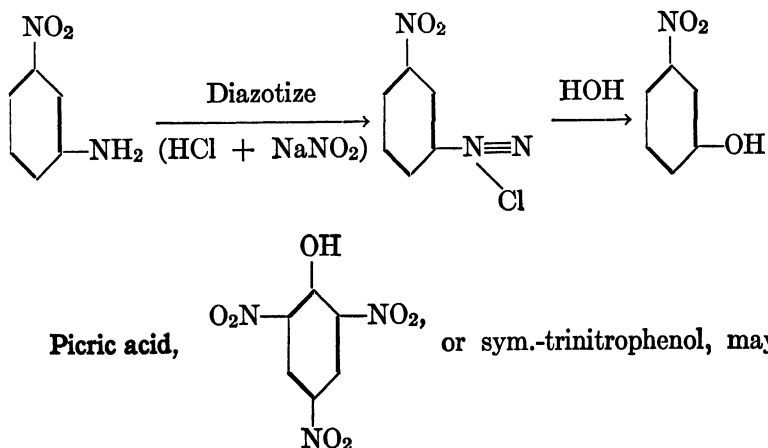
Of the three **nitroanilines**



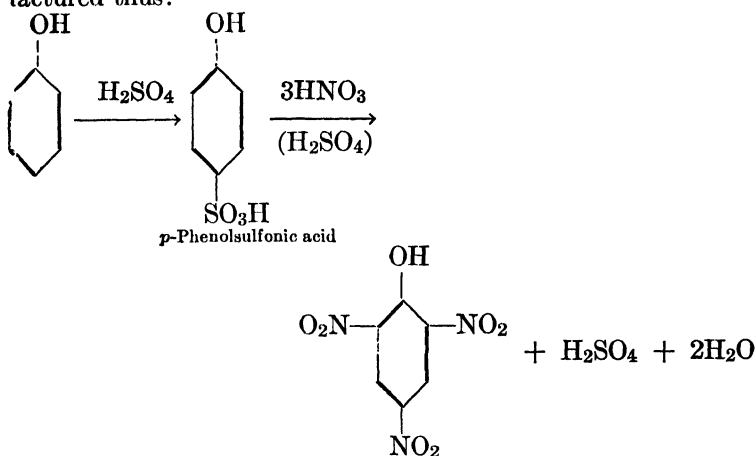
the second (*m*-variety) is prepared by treating benzene with nitric and sulfuric acids to produce the *m*-dinitrobenzene, and then employing a sufficiently mild reducing agent to reduce but one of the  $\text{NO}_2$  groups:



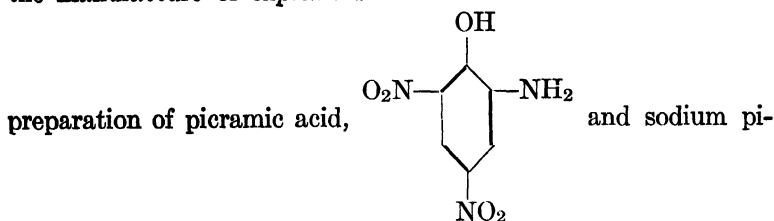
The *o*- and *p*-nitrophenols are prepared by direct nitration of phenol; the *m*- variety is prepared from *m*-nitroaniline:



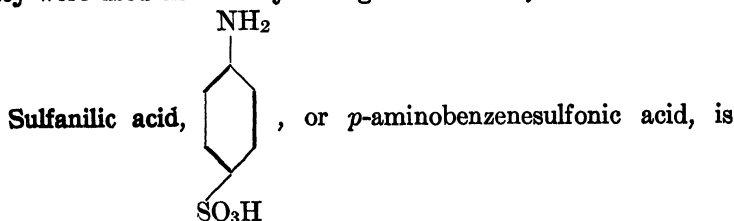
be prepared from phenol by nitration. Commercially, it is manufactured thus:



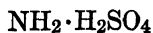
Picric acid is more strongly acidic than phenol, the increased acidity being due to the presence of the nitro groups. It is used in a colorimetric method for determining glucose in the blood, as a test for creatinine, as a precipitant for organic bases and proteins, as a "fixing" agent in histological work, in the treatment of the skin diseases and of burns, as an antiseptic, and in the manufacture of explosives. Picric acid is also used for the




cramate, which in turn are converted into several green and brown dyes. (Many of the nitro compounds of the aromatic series, such as picric acid and T.N.T.—p. 231—are powerful explosives. They were used extensively during the late war.)

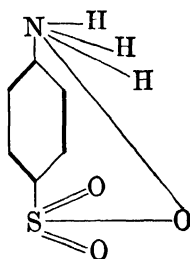


prepared from aniline by treatment with sulfuric acid, which first

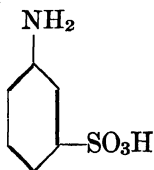


forms aniline acid sulfate, , and this on heating to 180° is

converted to sulfanilic acid. The acid is used in the manufacture of several dyes. (Since this compound contains a basic—NH<sub>2</sub>— and an acidic—SO<sub>3</sub>H—group, an “inner salt,” of the type



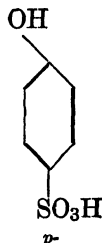
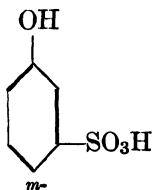
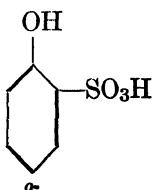
is possible. Compare with amino acids, p. 144.)



is **metanilic acid**. It is prepared by reducing

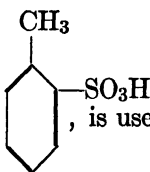
*m*-nitrobenzenesulfonic acid and is used in the preparation of azo dyes.

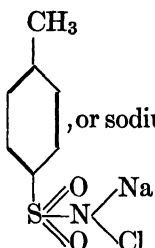
Of the **phenolsulfonic acids**,



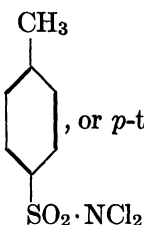
the *o*-variety is prepared by treating phenol with H<sub>2</sub>SO<sub>4</sub> (in the cold), the *p*-, by heating phenol with H<sub>2</sub>SO<sub>4</sub> to 96°, and the *m*-, by cautiously fusing (with NaOH) the *m*-benzenedisulfonic acid.

A mixture of the *o*- and *p*- is used as an antiseptic under the name "aseptol."

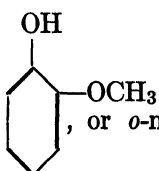
The *o*-Toluenesulfonic acid, , is used in the preparation of saccharin (p. 291).

Chloramine-T, , or sodium-*p*-toluenesulfon-*N*-chloramide

or "chlorazene" (a derivative of *p*-toluenesulfonic acid), is used as an irrigating fluid in the treatment of wounds, as a mouth wash, and, in general, as an active germicide. (It has approximately four times the antiseptic value of phenol.) It was introduced by Carrel and Dakin during the late war.

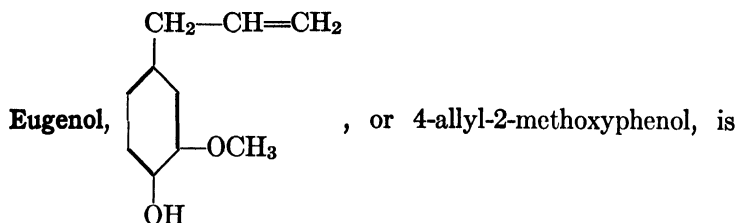
Dichloramine-T, , or *p*-toluenesulfon-*N*-dichloramide, is

also used in the treatment of infected wounds.

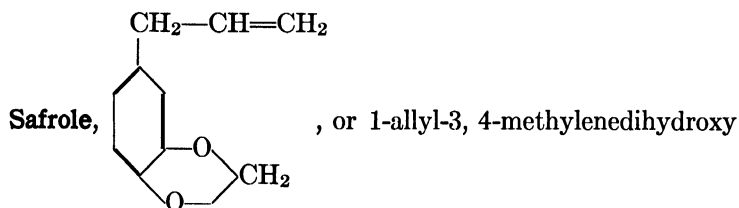
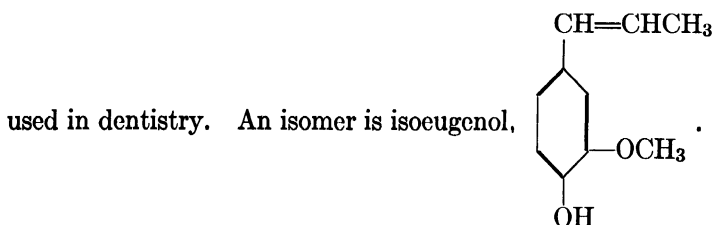
Guaiacol, , or *o*-methoxyphenol, or the monomethyl

ether of catechol, is found in gum guaiacum and in beechwood tar, and is obtained from guaiac resin by distillation. (The guaiac resin, dissolved in alcohol, is the "guaiac reagent" used in tests for oxidizing enzymes, blood, milk, etc.) Guaiacol, as well as some of its salts and esters, is used as internal antiseptic.

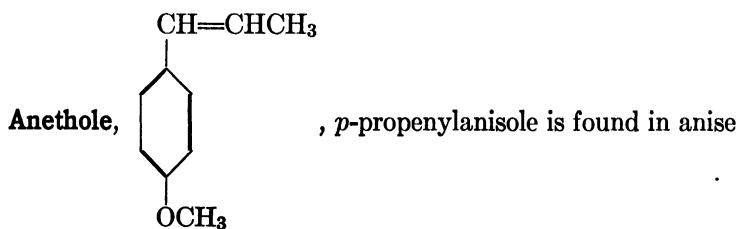




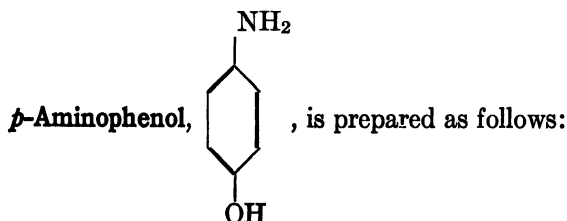
present in oil of cloves. It is an antiseptic and local anesthetic

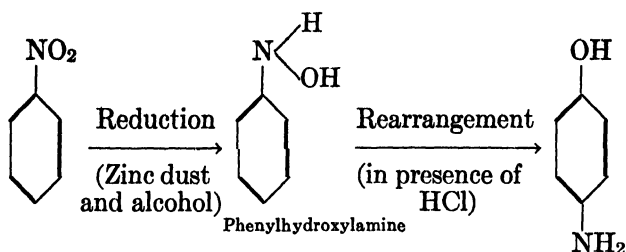


benzene is the chief constituent of oil of sassafras. It is used as an anodyne.



seed oil and is used as an antiseptic.

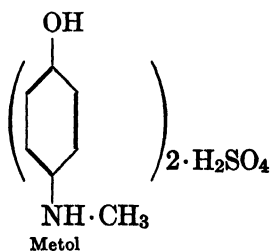
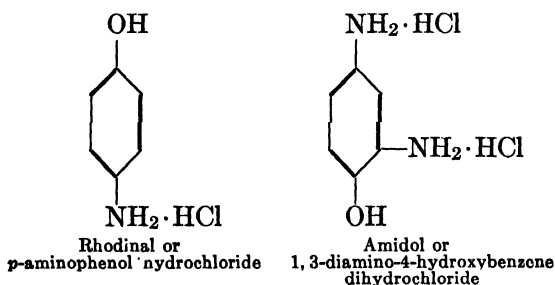




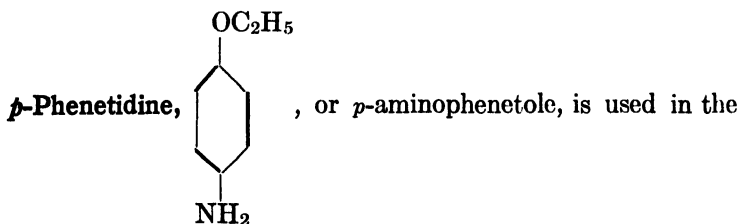
and is used as a photographic developer and in the manufacture

of such dye intermediates as *p*-hydroxydimethylaniline,

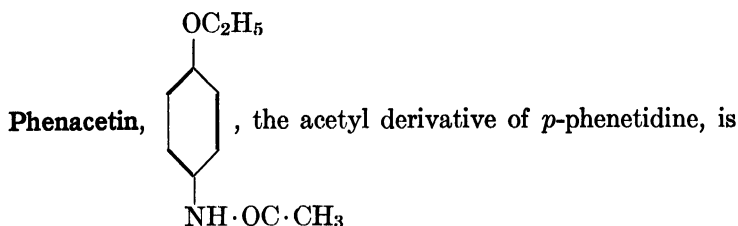
The 1, 4, or *p*-aminophenol type of compound and its derivatives make the best photographic developers. Some of the compounds used as photographic developers are:



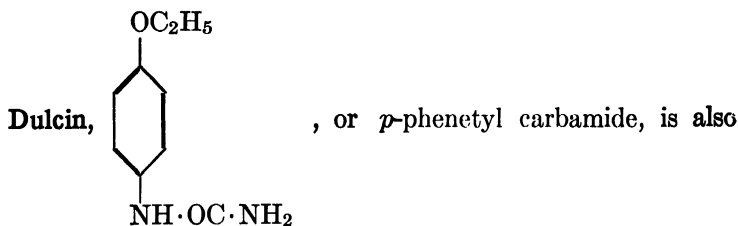
and there are number of others.



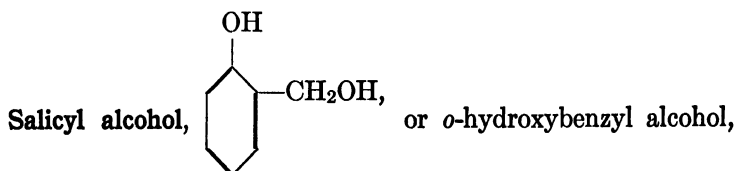
preparation of phenacetin, and often appears in the urine when phenacetin is administered.



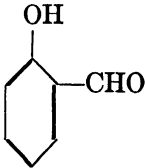
used as an antipyretic and analgesic.



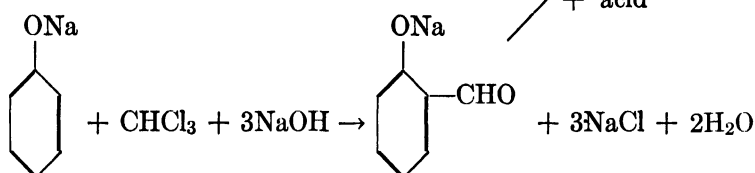
called "sucrol." It is two hundred times as sweet as cane sugar.



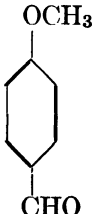
or saligenin occurs in combination with glucose in the glucoside salicin (present in willow bark). It has been recently recommended as a local anesthetic.

Salicylaldehyde, , or *o*-hydroxybenzaldehyde, is

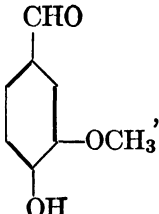
prepared by the *Reimer-Tiemann* reaction:



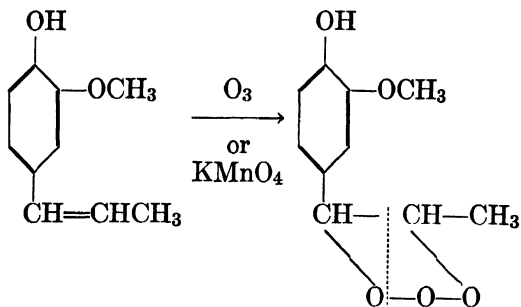
(The *p*-modification is also produced, but the *o*- and *p*- can be separated by steam distillation, the *o*- passing over with the steam.) This aldehyde occurs in oil of spiroca and oil of certain flowers and is used in perfumery and in the preparation of coumarin (p. 309).

Anisaldehyde, , or *p*-methoxybenzaldehyde, is found

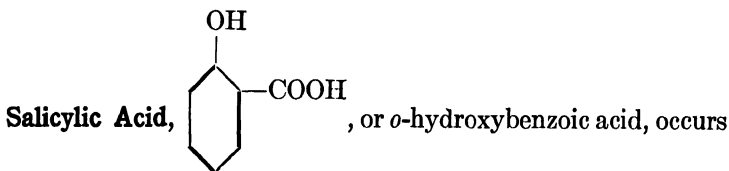
in anise seed oil and is used in perfumery.

Vanillin, , or *m*-methoxy-*p*-hydroxybenzaldehyde,

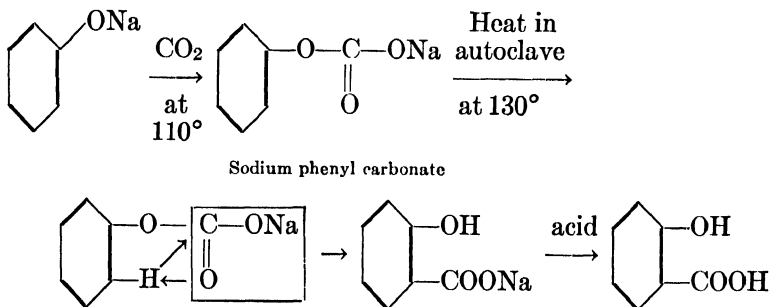
is present in vanilla bean and is the chief constituent of extract of vanilla. It is manufactured by the oxidation of isoeugenol:



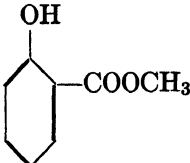
and also from guaiacol by the *Reimer-Tiemann* reaction (see above). It is used in perfumery, as a flavoring agent and as a gastric stimulant.



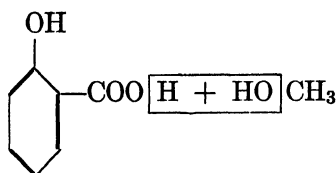
in blossoms of meadow sweet, and, as its methyl ester in oil of wintergreen. It is prepared by the *Kolbe-Schmitt* reaction:



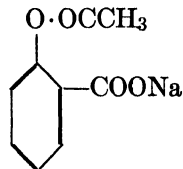
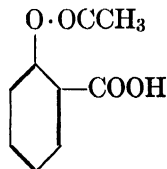
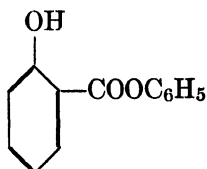
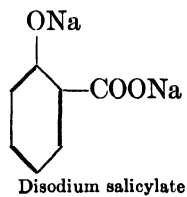
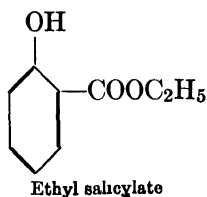
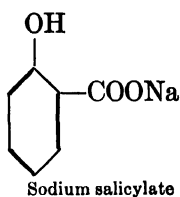
Salicylic acid is sometimes used in medicine for the treatment of rheumatic diseases, to check gastric fermentation and also as an antipyretic and intestinal antiseptic. It is most commonly administered in the form of some of its derivatives, such as salol, aspirin, sodium salicylate, strontium salicylate and methyl salicylate. It is employed to some extent in the preparation of corn cures and skin disease salves. Large quantities are used in the manufacture of dyestuffs.

**Methyl salicylate**, , is the chief constituent

of "oil of wintergreen," and is the artificial oil of wintergreen. It is prepared by heating salicylic acid with methanol (esterification):

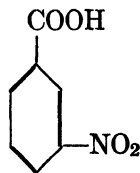
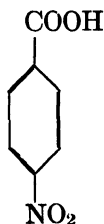
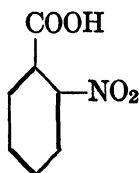


A number of the salicylates, and their derivatives, such as

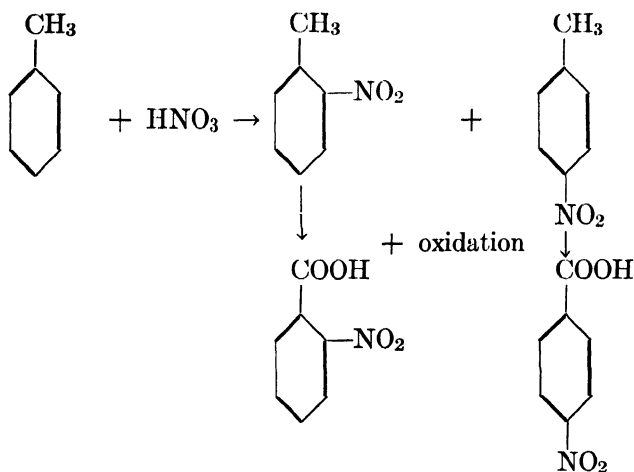


are used as intestinal antiseptics and as antipyretics.


There are three isomers of **nitrobenzoic acid**:





the first two being prepared from toluene; e.g.,



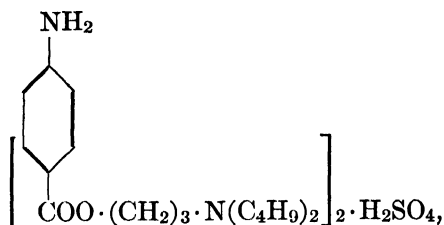
and the *m*-variety, by direct nitration of benzoic acid. On reduction they yield the corresponding amino acids.

A number of derivatives of *p*-aminobenzoic acid,  are

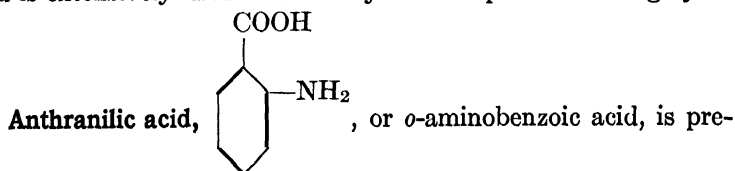
important local anesthetics. Anesthesine is , ethyl

*p*-aminobenzoate. Novocaine is   $\text{COO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{N}(\text{C}_2\text{H}_5)_2 \cdot \text{HCl}$ .

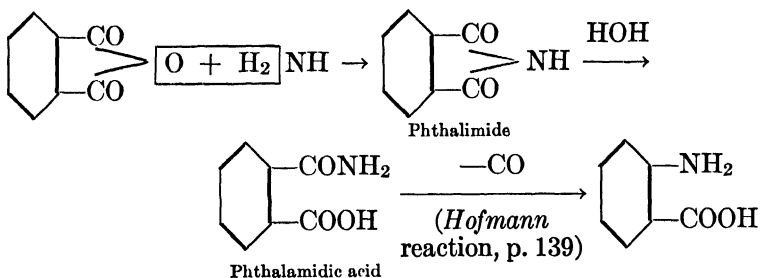
It is only one-seventh as toxic as cocaine. Procaine is another name for novocain. Butyn is



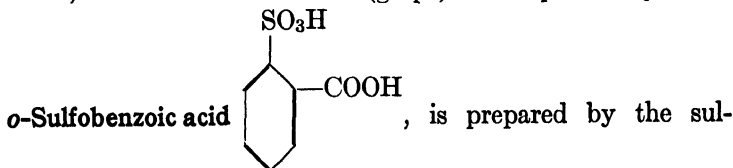
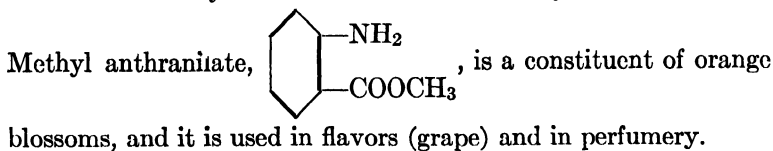
and is extensively used in dentistry and in ophthalmic surgery.



pared either from *o*-nitrobenzoic acid by reduction, or from phthalic anhydride:

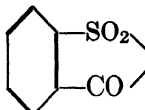


It is used as a dye intermediate and in the synthesis of indigo.

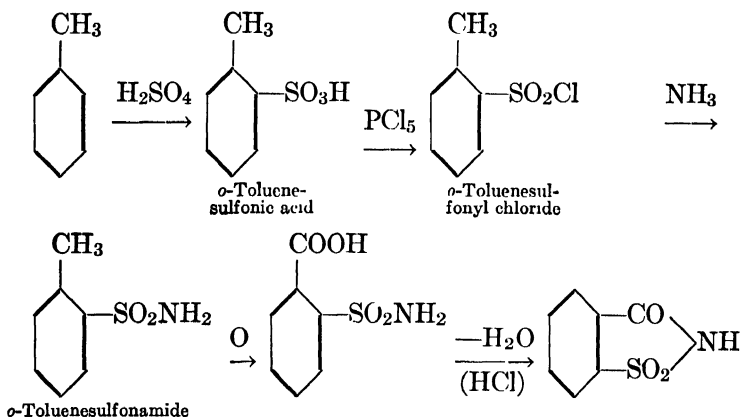


fonation of toluene and the subsequent oxidation of the  $\text{CH}_3$  group.

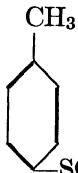


Saccharin, , or *o*-benzoic sulfonide, may be

prepared as follows:

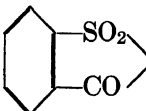


(When toluene is sulfonated a mixture of *o*- and *p*-compounds is, of course, formed. These are separated at the sulfonyl-

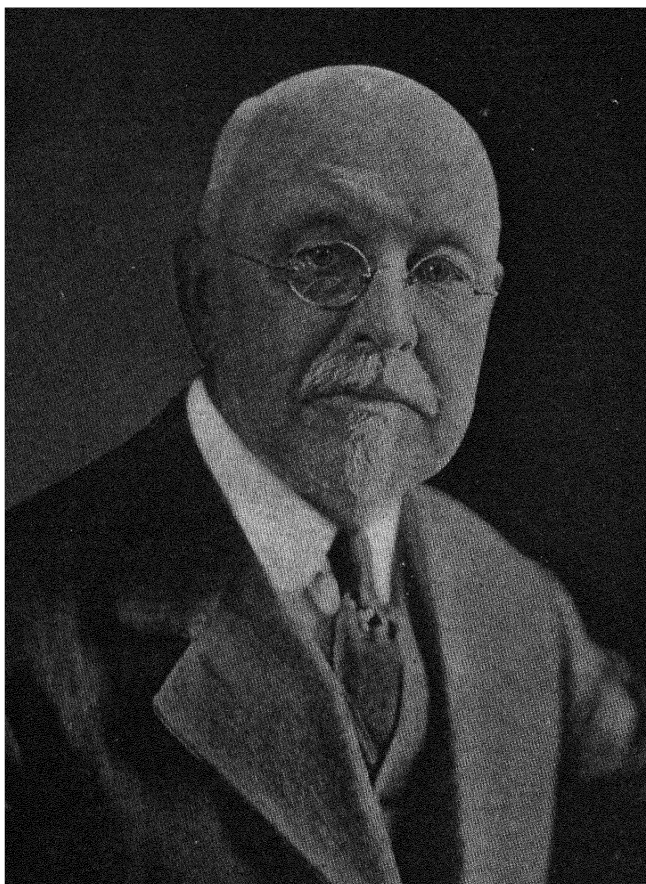
chloride stage  by filtering them with ice, the *p*-com-

pound, being a solid at that temperature, remains on the filter, the *o*- going through in the form of a thick, oily liquid.)

Saccharin was first prepared by Remsen. It is said to be about 550 times as sweet as sugar, and is used as a substitute for sugar in diabetes, and as sweetening agent in mouth-washes, tooth-pastes, etc. The substance has no nutritive value. (Since saccharin itself is not very soluble in water, the sodium salt

, which is very soluble, is manufactured.)

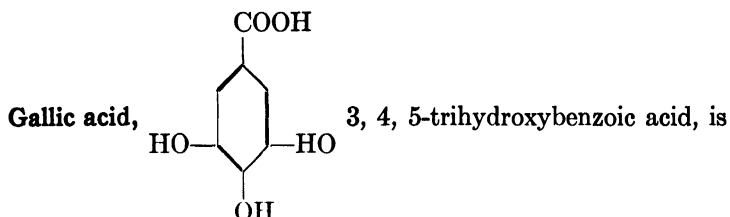
*p*-Toluenesulfonylchloride, is employed with *p*-toluenesulfonamide as a camphor substitute. *p*-Toluenesulfonic acid is also used in the manufacture of dyes. *p*-Toluenesulfonamide is employed in the preparation of chloramine-T.



*Ira Remsen.*

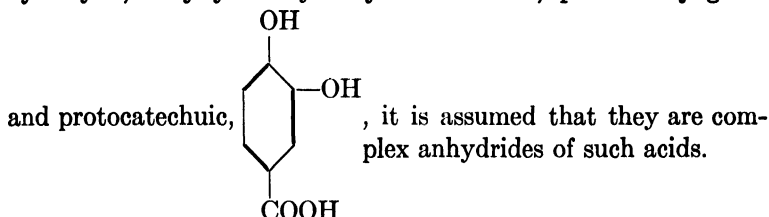
IRA REMSEN (1846-1927)

FOR MANY YEARS PROFESSOR OF ORGANIC CHEMISTRY AT JOHNS HOPKINS UNIVERSITY (AND LATER ITS PRESIDENT), IS BEST KNOWN FOR HIS WORK ON SACCHARIN (P.291) AND AS THE AUTHOR OF TEXT-BOOKS ON ORGANIC CHEMISTRY. HE HAS DONE MUCH TO FURTHER RESEARCH IN ORGANIC CHEMISTRY IN THIS COUNTRY.



found free, or as a glucoside in a number of plants (sumach, gall nuts, etc.), and may also be obtained by hydrolyzing tannins with acid. When heated,  $\text{CO}_2$  is evolved and pyrogallic acid is formed (p. 255). Gallic acid is used in photography, ink and as an astringent.

**Tannic acids.**—These acids are found in gall nuts and other plants. Their exact constitution is not known, but since, on hydrolysis, they yield hydroxybenzoic acids, particularly gallic



The mother substances of these tannic acids are tannins, which are glucosides. (The names "tannic acid" and "tannins" are commonly used interchangeably.) These tannins are found in gall nuts, oak, chestnut, pine, hemlock, etc. They give characteristic blue-black or green-black colors with ferric chloride and are valuable astringents. They precipitate proteins and alkaloids. They are largely employed in the making of leather, as mordants in dyeing, and in the manufacture of inks.

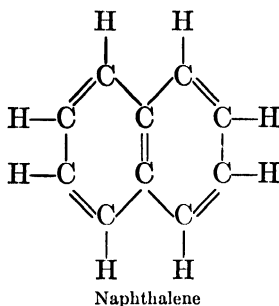
#### READING REFERENCES

- TILDEN—Chemical Discovery and Invention in the Twentieth Century. (1916), chap. 22 (Drugs).  
 FISCHER—Synthesis of Depsides, Lichen Substances and Tannins. *Journal of the American Chemical Society*, **36**, 1170 (1914).  
 HARROW—Eminent Chemists of Our Time. (1927), chapters dealing with Reimsen.  
 BROWN—Forest Products. (1919), chap. 3 (Tanning).  
 CLARK—Applied Pharmacology. (1923), pp. 80–84 (The Action of Salicylates).  
 GILMAN—Local Anesthetics. *Journal of Industrial and Engineering Chemistry*, **14**, 812 (1922).

## CHAPTER XXVIII

### NAPHTHALENE, ANTHRACENE AND THEIR DERIVATIVES

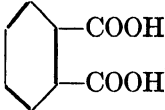
So far we have considered aromatic compounds containing the benzene nucleus; but now we begin to discuss compounds containing two or more condensed benzene rings, in which—to take an example—two carbon atoms are common to both rings:




Naphthalene and anthracene are the most important of such compounds.

**Naphthalene.**—This hydrocarbon is obtained from coal tar in the fraction distilling over between 170–230° (middle or carbolic oil fraction. See chart facing p. 211); the crude product so obtained is purified by sublimation. Naphthalene crystallizes in lustrous plates, having a m.p. of 80° and a b.p. of 218°. It is very volatile and has a characteristic odor. It is used in the preparation of naphthalene compounds, in moth-balls, as an insecticide and germicide, in the manufacture of phthalic anhydride (p. 273), and dye intermediates (p. 311).

Naphthalene has the formula  $C_{10}H_8$  and on oxidation yields

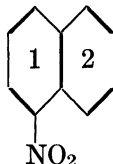
phthalic acid, , which proves the hydrocarbon to

contain a benzene ring, as well as some side-chains containing two carbon atoms in the *o*-position with respect to one another. That the actual constitution of naphthalene corresponding to

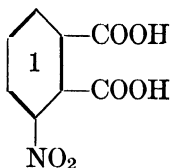
$C_{10}H_8$  is  or two condensed benzene rings, is suggested

by a number of reactions, of which two will be mentioned.

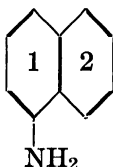
Naphthalene, like benzene, can be readily nitrated, yielding nitronaphthalene, and the latter reduced, giving aminonaphthalene. When nitronaphthalene is oxidized, we get nitrophthalic acid, but when aminonaphthalene is oxidized, we do not get aminophthalic acid, but just phthalic acid. If we write the structure for nitronaphthalene as



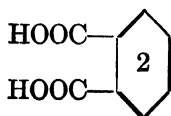
then it is plain that on oxidation, ring (2) must be oxidized to yield nitrophthalic acid



whereas if we write aminonaphthalene as

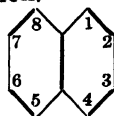


then it is equally evident that ring (1) must here be oxidized to yield phthalic acid

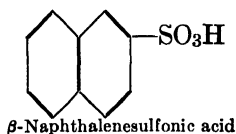
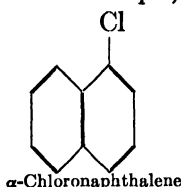


Obviously, then, there must be two benzene rings in naphthalene—two benzene rings having two carbon atoms in common.

Naphthalene has 8 replaceable hydrogen atoms:

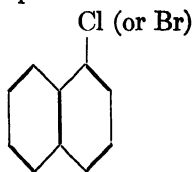


Since the molecule is symmetrical in structure, positions 1, 4, 5 and 8 are identical, and positions 2, 3, 6 and 7 are identical. We, therefore, have two possible monosubstitution products, a substituent at position 1 (or 4, 5, 8) being known as  $\alpha$ - (*alpha*), and a substituent at position 2 (or 3, 6, 7) being known as  $\beta$ - (*beta*). For example,

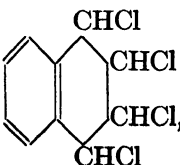


With disubstitution products, where the substituents are the same, 10 isomers are possible: 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 2:3, 2:6, 2:7; but where they are dissimilar, 14 isomers become possible. Many substitution products and derivatives of naphthalene are manufactured, since they are used as dye intermediates, but only a few of these will be discussed here.

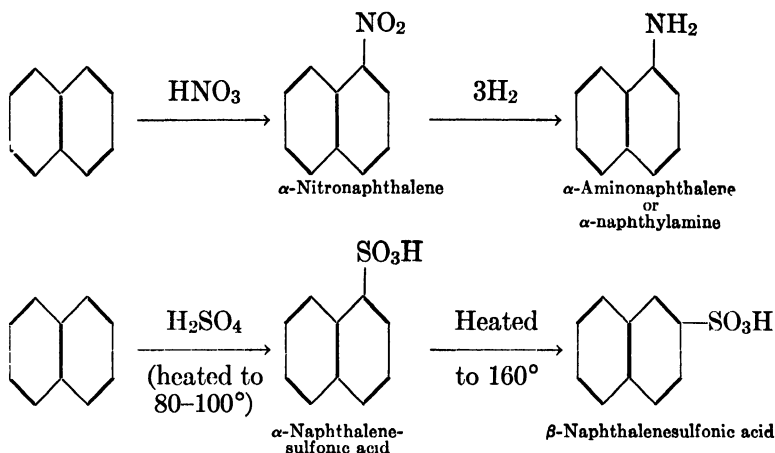
$\alpha$ -Chloro (or bromo) naphthalene



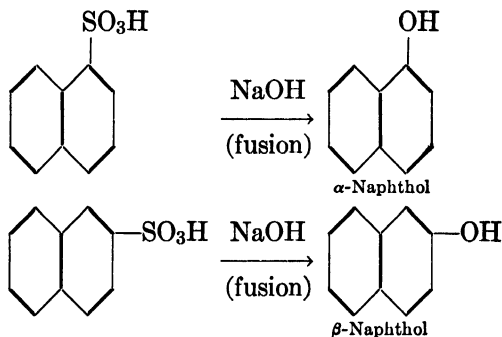
is prepared by the direct action of chlorine (or bromine) on boiling naphthalene. (The  $\beta$ -chloro—or bromonaphthalene—is prepared by indirect methods.) On the other hand, when chlorine (from potassium chlorate and HCl) is allowed to act on the hydro-

carbon, naphthalene tetrachloride,  an addition product is obtained.

Some other reactions are:

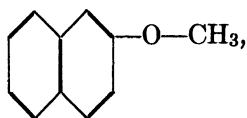


The sulfonic acids are used in the manufacture of naphthols:



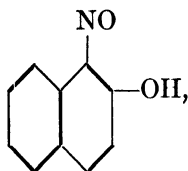
These reactions, it will be noticed, are entirely analogous to the preparation of phenol from benzenesulfonic acid (see p. 229). The naphthols are very important dye intermediates.  $\alpha$ -naphthol is also used to test for the presence of carbohydrates (p. 172).

$\beta$ -naphthol is employed internally as an intestinal antiseptic, and externally, in the form of ointment, for the treatment of skin diseases.

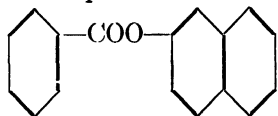


$\beta$ -naphthyl methyl ether is known as

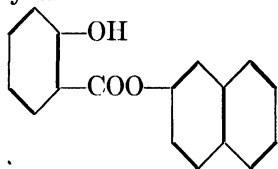
synthetic "yara-yara" and is used in perfumery. The  $\beta$ -naphthyl ethyl ether is known as synthetic "nerolin" and is also used in perfumery.



$\alpha$ -nitroso- $\beta$ -naphthol is used to determine cobalt in quantitative analysis.

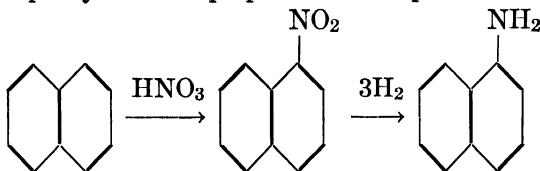


$\beta$ -naphthyl benzoate is used internally as an intestinal antiseptic in diarrhea and typhoid fever.

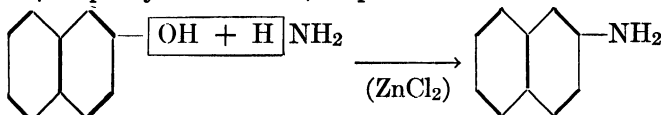


$\beta$ -naphthyl salicylate is useful in intestinal fermentations.

$\alpha$ -Naphthylamine is prepared from naphthalene:



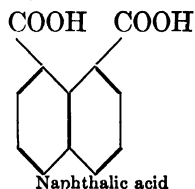
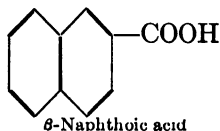
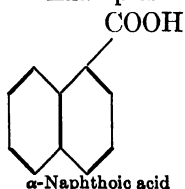
and  $\beta$ -naphthylamine from  $\beta$ -naphthol:



The  $\beta$ -naphthylamine may also be obtained by heating  $\beta$ -naphthol with ammonium chloride and NaOH in an autoclave at  $160^\circ$ . The naphthylamines are used extensively for the manufacture of dye intermediates and azo dyes (p. 325).

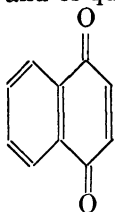
(Just as the  $\text{NH}_2$  group in aniline, etc., can be diazotized—see p. 241—so can the  $\text{NH}_2$  group in naphthalene compounds.)

Examples of acids derived from naphthalene are:

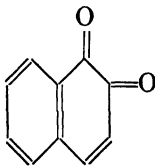




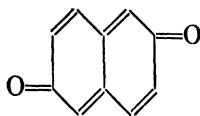
and of quinones:



$\alpha$ -Naphthoquinone



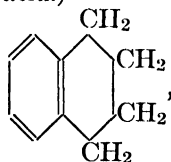
$\beta$ -Naphthoquinone



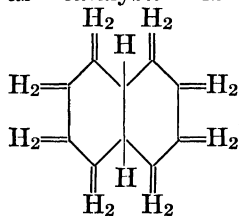
Amphi-Naphthoquinone

(The  $\alpha$ -variety may be prepared by oxidizing naphthalene with chromic acid in the presence of glacial acetic acid.)

("Tetralin," or naphthalene tetrahydride,



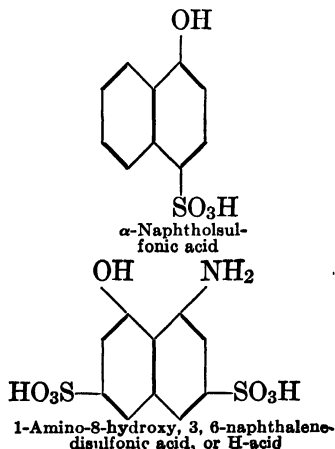
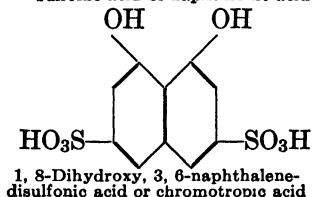
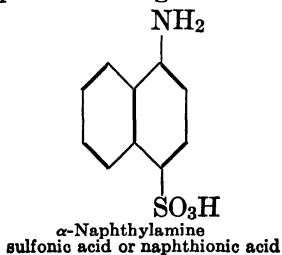
which has been suggested as a motor fuel and solvent, is prepared by reducing naphthalene with hydrogen in the presence of nickel as catalyst. A somewhat similar compound, "decalin,"



, has also been suggested as motor fuel and

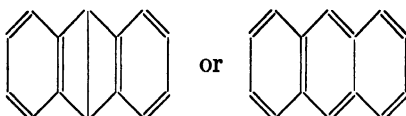
solvent. They are also used in textile soaps and in detergents.

Many dye intermediates containing different substituents in the naphthalene ring are manufactured. A few of these are:

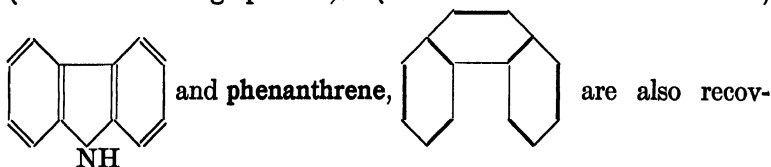




**Anthracene**,  $C_{14}H_{10}$ , or



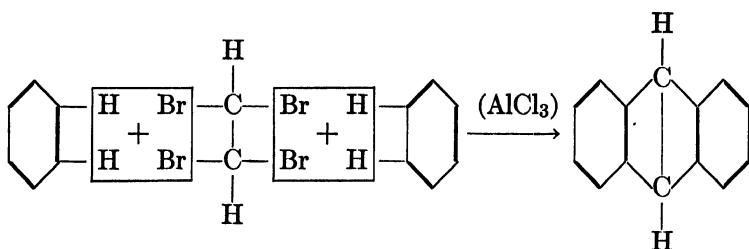
is separated from coal tar in the fraction which boils over  $270^\circ$  (see chart facing p. 211). (From this fraction **carbazole**,



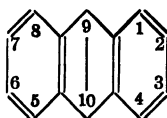
ered).

The process by which this hydrocarbon is purified is a rather laborious one. The final purification is carried out by sublimation with superheated steam (m.p.  $216^\circ$ , b.p.,  $360^\circ$ ). Anthracene comes in the form of colorless, glistening leaflets, having a blue fluorescence. It is used in the manufacture of anthraquinone and its derivatives.

The structure of anthracene has been confirmed by a number of syntheses of the compound, one of which will be given: In the presence of  $AlCl_3$ , two molecules of benzene combine with one molecule of tetrabromoethane to form anthracene (*Friedel-Crafts reaction*.)

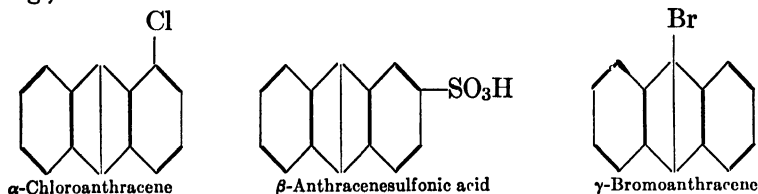


The positions of the replaceable hydrogen atoms are numbered thus:

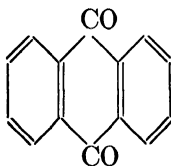


and from its structure it may be seen that positions 1, 4, 5 and 8 bear exactly the same relationship to the molecule. This is also

true of positions 2, 3, 6 and 7, and of 9 and 10. There are possible, therefore, three mono-substitution products; 1, 4, 5 or 8—being known as  $\alpha$ -; 2, 3, 6 or 7, as  $\beta$ ; and 9 or 10 as  $\gamma$  (gamma); e.g.,



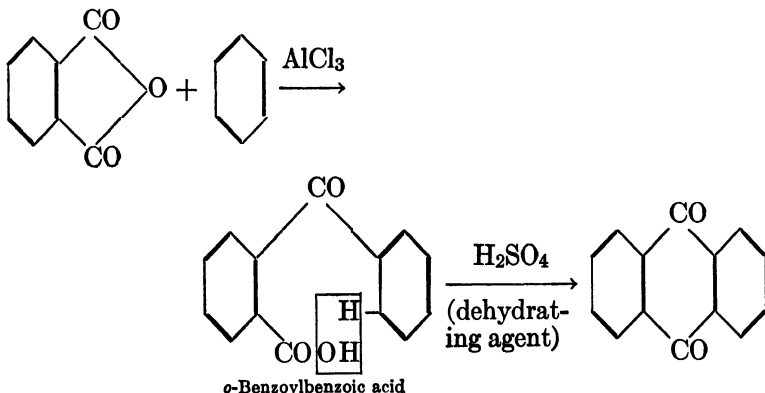
The most important derivative of anthracene is anthraquinone,



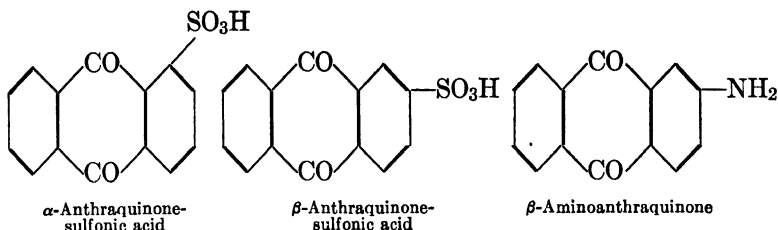
which is prepared from anthracene by oxidation with chromic acid ( $\text{Na}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$ ).

(Nitric acid does not give rise to nitro-derivatives with anthracene, but converts it to anthraquinone—an indication that the central nucleus in anthracene is somewhat different from the two outer benzene nuclei.)

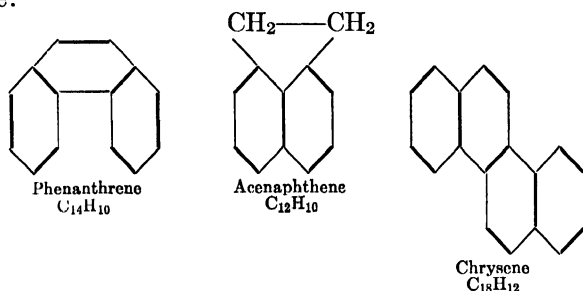
Anthraquinone is manufactured on a large scale, for it is used in the manufacture of dyes (such as alizarin) and dye intermediates. It is synthetically produced from phthalic anhydride by condensing the latter with benzene.



A number of other important anthraquinone derivatives used in the manufacture of dyes are:



A few other condensed ring compounds obtained from coal tar are:



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KLIPSTEIN—The Development of Synthetic Anthraquinone. *Industrial and Engineering Chemistry*, **18**, 1327 (1926).

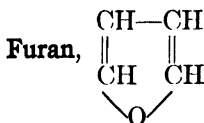
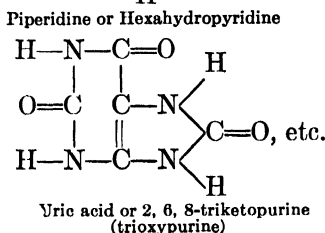
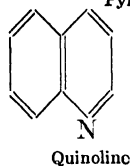
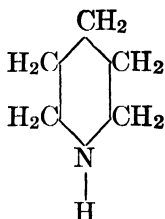
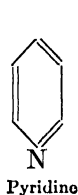
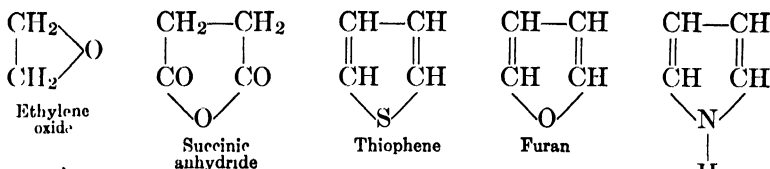
PHILLIPS—Chemistry of Anthraquinone. *Chemical Reviews*, **6**, 157 (1929).

A careful survey of the compounds so far studied will reveal that they have been prepared by making use of one or more of the following type reactions: halogenation, reduction, alkylation, oxidation, condensation, nitration, sulfonation, amidation, alkali fusion, nitrosation, hydrolysis, internal rearrangement, etc. Many of the substances prepared in this way are classed as dye "intermediates" and are used in the preparation of dyes, which are taken up in Chapter XXX.

## CHAPTER XXIX

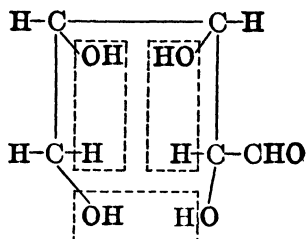
### HETEROCYCLIC COMPOUNDS

THE "cyclic" or "ring" compounds so far considered, with a few exceptions, such as succinic anhydride, lactones, etc., have contained the same elements within the ring (in this particular case, carbon atoms; hence **carbocyclic**). There are, however, very many compounds containing "cycles" in which elements other than carbon are also present; these are known as **heterocyclic**, for example,



, or furfuran, occurs in pinewood tar. Its most important derivative is **furfural**,  $\begin{array}{c} \text{CH}-\text{CH} \\ || \quad || \\ \text{CH} \quad \text{C}-\text{CHO} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$ , or furfural-

aldehyde, which may be obtained from a pentose sugar, or pentosans, when boiled with hydrochloric or sulfuric acid (see p. 167):



(This serves as the basis for the detection and estimation of pentoses and pentosans.) Commercially, furfural is prepared from corn and maize cobs, oat hulls, and other waste cereal products rich in pentoses or pentosans. It is used in the manufacture of synthetic resins, disinfectants, deodorizers, solvents, paint and varnish remover, etc. The general properties of furfural are similar to those of benzaldehyde. On oxidation, we get pyromucic

acid,  $\begin{array}{c} \text{CH}-\text{CH} \\ \parallel \quad \parallel \\ \text{CH} \quad \text{C}-\text{COOH} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$ , which, as its name implies, may also be

prepared by heating mucic acid,  $\text{COOH} \cdot (\text{CHOH})_4 \cdot \text{COOH}$ , an oxidation product of galactose (p. 177) or lactose. (The *Molisch test* for carbohydrates—p. 172, is said to be dependent upon the production of furfural or its derivatives.)

**Pyrrole**,  $\begin{array}{c} \text{CH}-\text{CH} \\ \parallel \quad \parallel \\ \text{CH} \quad \text{CH} \\ \diagdown \quad \diagup \\ \text{N} \\ | \\ \text{H} \end{array}$ , is present in coal tar and in bone oil

(Dippel's oil), which is a product of the destructive distillation of bones. (The pyrrole ring is present in a number of alkaloids.)

It may be reduced to **pyrrolidine**,  $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ | \quad | \\ \text{CH}_2 \quad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{N} \\ | \\ \text{H} \end{array}$ , a carboxylic acid


derivative of which is **proline**,  $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ | \quad | \\ \text{CH}_2 \quad \text{CH} \cdot \text{COOH} \\ \diagdown \quad \diagup \\ \text{N} \\ | \\ \text{H} \end{array}$ . one of the decom-

position products of proteins (p. 152). Pyrrole compounds may be



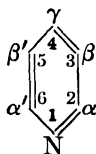


(thiophene is readily sulfonated, while benzene is not), and may be identified by the "indophenin" reaction (a mixture of isatin, thiophene and  $\text{H}_2\text{SO}_4$  gives a blue color).

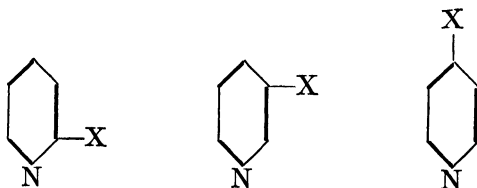
**Pyridine,**  (which may be looked upon as benzene in

which one CH is replaced by N), is found in coal tar in the "light oil" fraction, in tobacco smoke, in *Dippel's* oil, and in crude ammonia. Pyridine is soluble in water, the solution being slightly alkaline in reaction. It has a characteristic, putrid odor and is an extremely stable substance, not being attacked by chromic acid ( $\text{CrO}_3$ ) or nitric acid. It is used to denature alcohol. (The pyridine ring is present in a number of alkaloids.)

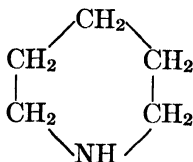
The positions in pyridine are numbered

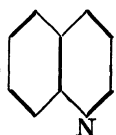


The compound has three mono-substitution products of the type

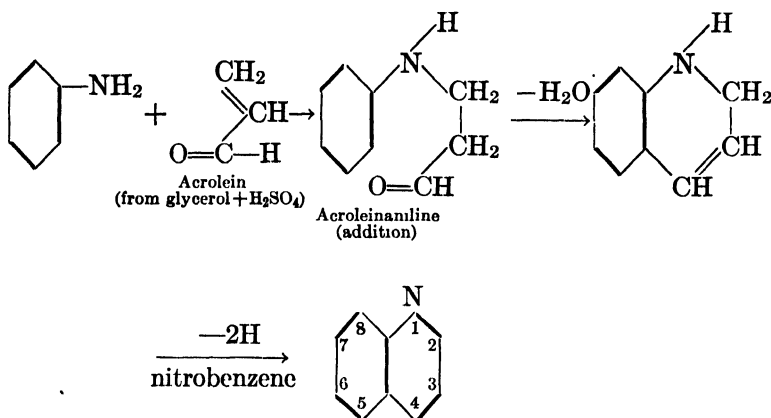


When reduced, pyridine yields **piperidine**, a substance which occurs in pepper and has a pepper-like odor.

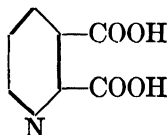


**Quinoline,** , a condensation of one benzene and one

pyridine ring, is present in coal tar and bone oil, and may be prepared by the *Skraup's* reaction, in which a mixture of aniline, glycerol,  $\text{H}_2\text{SO}_4$  (dehydrating agent) and nitrobenzene (oxidizing agent) are heated:



On oxidation, quinoline yields quinolinic acid,




(What does naphthalene yield on oxidation?)

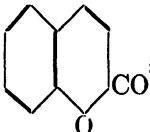
(The quinoline ring is present in certain alkaloids.)

A quinoline derivative known as "plasmochin" has been introduced as a new remedy for malaria.

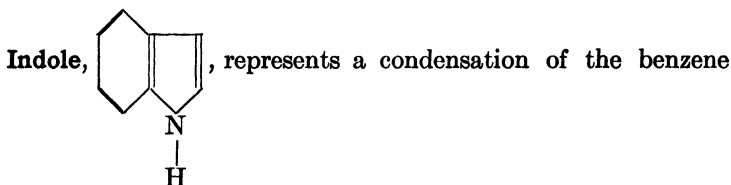
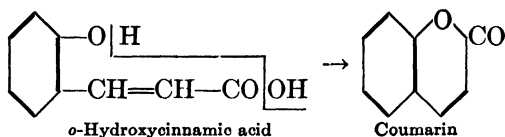
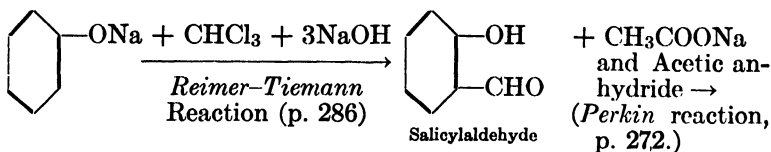
8-Hydroxyquinoline is used in the quantitative determination of metals, especially aluminum.

**Isoquinoline**, , is found in coal tar. (The iso-

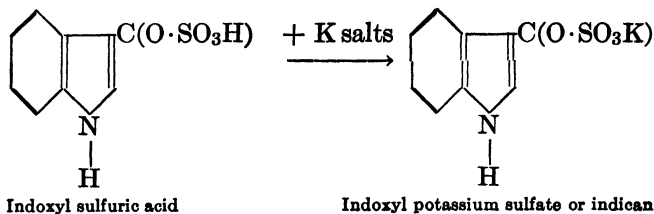
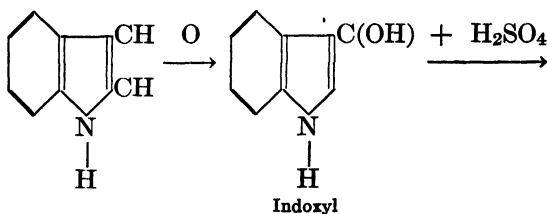
quinoline grouping is present in a number of alkaloids.)

**Coumarin**, , is the sweet-smelling constituent of

tonka bean, and freshly-mown hay. It is used extensively in flavoring extracts, flavoring tobacco, perfumery and as an adulterant for vanillin. It is made by the following series of reactions:

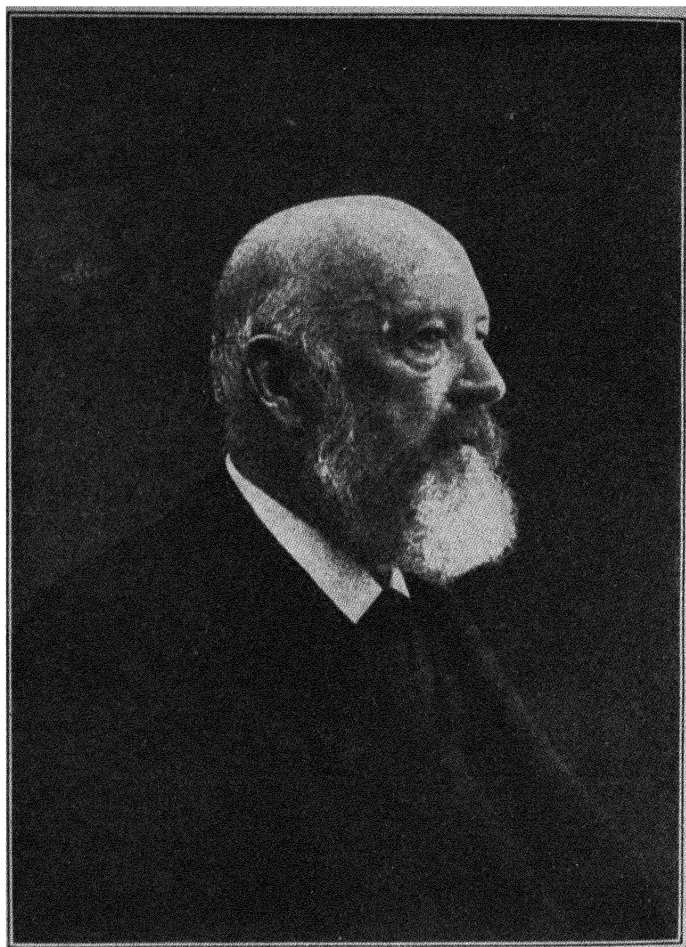


and pyrrole rings, and is an intestinal product formed when proteins putrify. Indole is a highly toxic substance and is de-toxified by being converted into indican, in which form it is eliminated in the urine:



(The amount of indican in the urine is a rough indication of the extent of putrefaction within the intestine.)

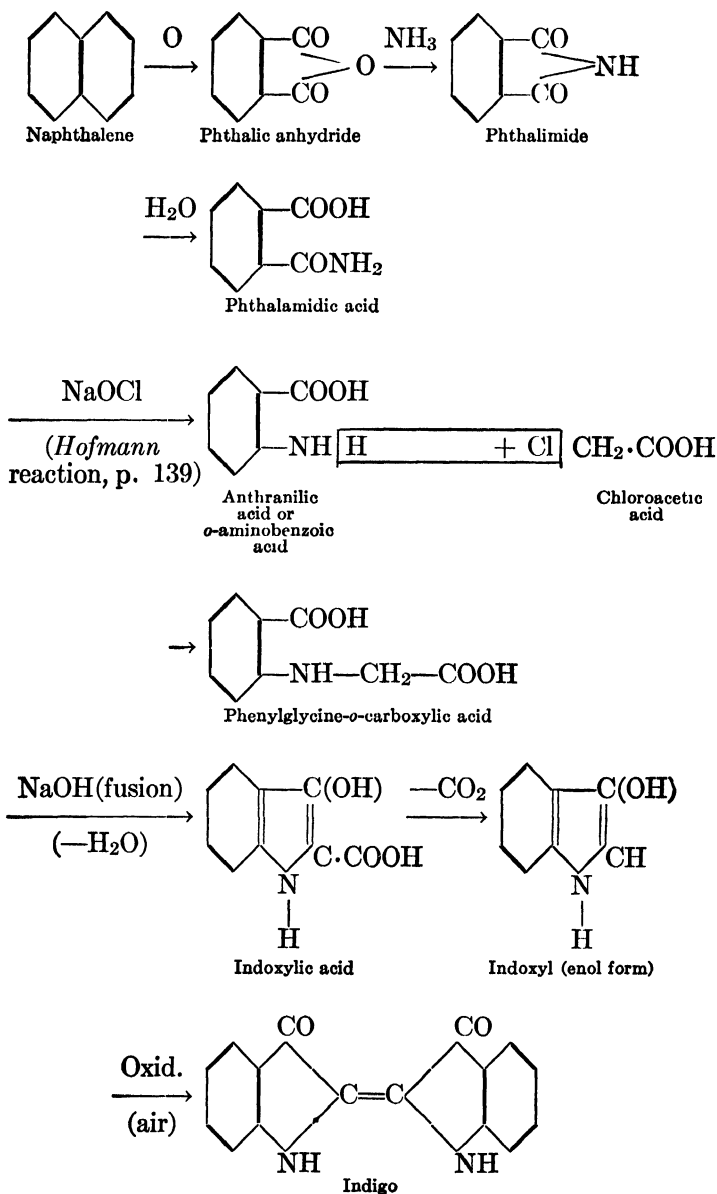
**Indigo** is a natural product obtained from the indigo plant (in which it occurs as the glucoside "indican")—which grows in tropical countries—and is one of the oldest and best known vat dyes. Its synthesis in the chemist's laboratory (by Baeyer)



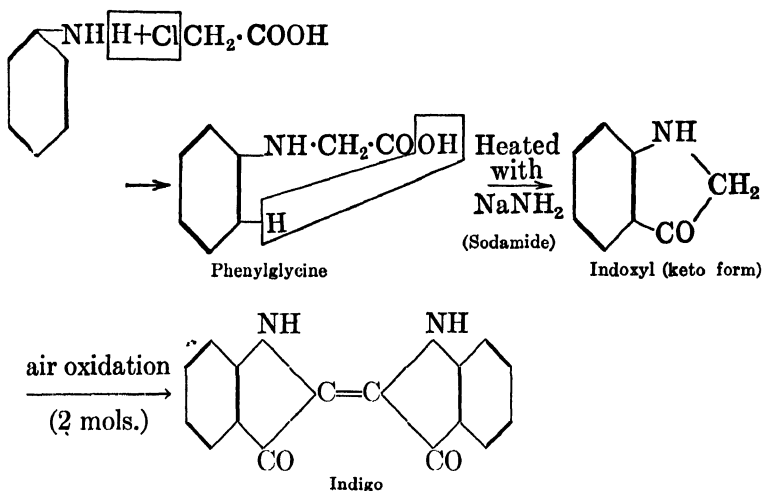
*Adolf Bayer*

JOHANN FRIEDRICH WILHELM ADOLF BAEYER (1835-1917)  
RESPONSIBLE FOR THE SYNTHESIS OF INDIGO (P. 309), WAS ONE OF THE MOST  
FRUITFUL WORKERS IN ORGANIC CHEMISTRY DURING THE NINETEENTH CENTURY.

ranks as one of the great achievements in the history of organic chemistry. It may be produced artificially by the following series of reactions:

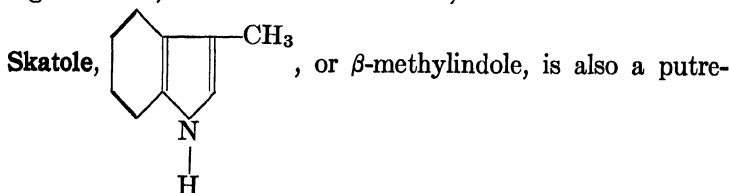


On a commercial scale at the present time, indigo is prepared as follows:

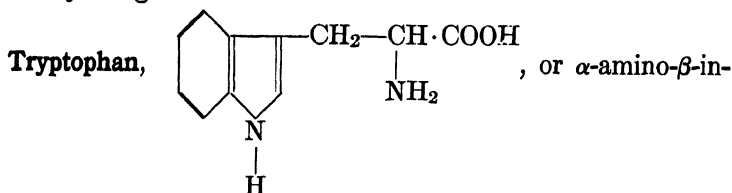


Prior to the World War the production of synthetic indigo accounted for 28 per cent of the total production of coal-tar dyes. Despite the fact that there are over one thousand chemically different dyes now in commercial production, indigo has maintained its position as the leader in quantity.

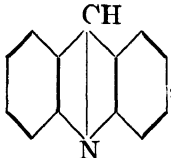
(The disodium salt of indigodisulfonic acid, known also as "indigo carmine," is used as a food color.)

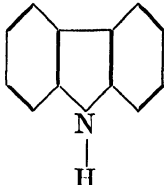


factive product formed in the intestine and its fate in the body is similar to that of indole. It is present in feces and has an extremely disagreeable odor.



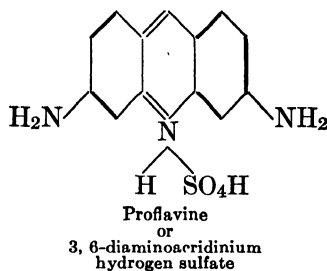
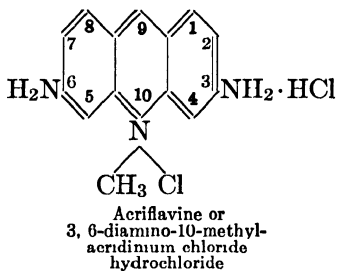
dolepropionic acid, has already been referred to under amino acids (p. 148).

Two other heterocyclic compounds are **acridine**, ,

present in coal tar, and **carbazole**,  or dibenzopyr-

role, present in anthracene oil. Carbazole is used in the manufacture of dyes.

Two important derivatives of acridine have recently been introduced in medicine:



They are strongly antiseptic and non-toxic.

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## CHAPTER XXX

### DYES AND STAINS

#### DYES

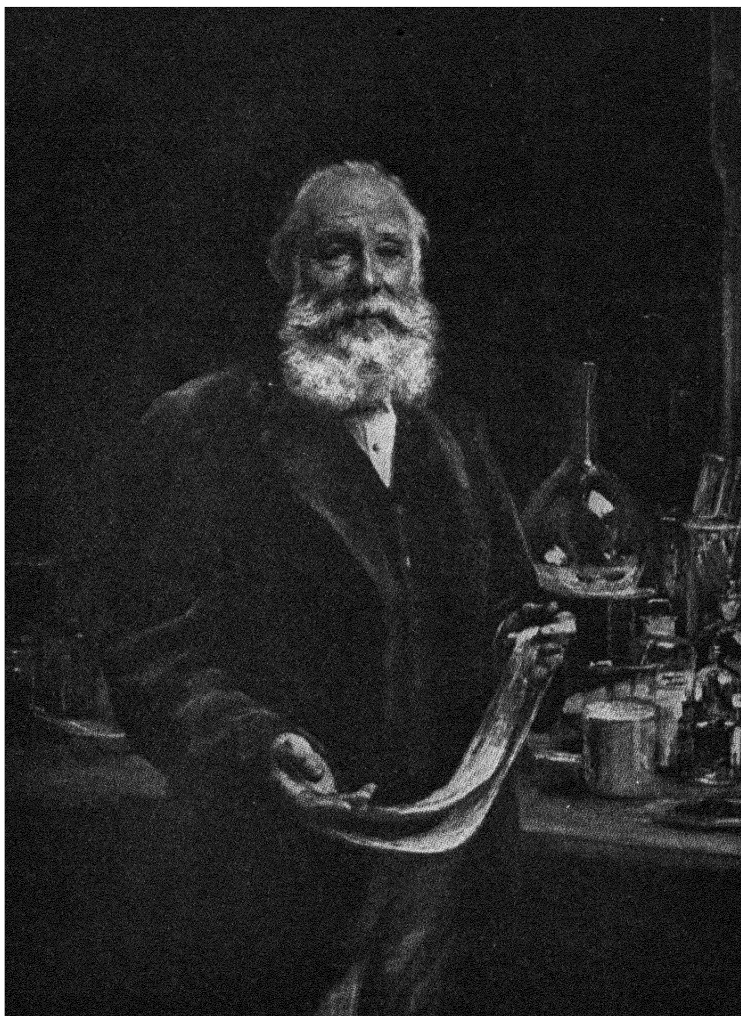
DYES have a wide application. They are applied to cotton, linen, silk, wool, paper, straw, wood, leather, feathers, hair, fats, waxes, soaps, inks, food, condiments (jams, macaroni, candy), varnishes, paints, etc. In analytical chemistry, dyes are used as indicators (e.g., phenolphthalein, congo red, methyl orange). In histology and bacteriology, they are used for staining microscopical preparations (e.g., methylene blue, acid fuchsin, safranine, eosin, gentian violet, neutral red, Bismarck brown). Dyes are also used as explosives (picric acid, picrates, trinitrocresols, etc.); in photography (eosin, erythrosin, etc.); as antiseptics (acriflavine, proflavine, malachite green, mercurochrome-220, etc.); in geographic and sanitary investigations, dyes (eosin, fluorescein) have been used to reveal whether any connection existed between flowing waters, sewage contamination, etc.

Dyes have been used from the very earliest times. Until the middle of the last century, those used for dyeing and printing were the vegetable dyes, coloring substances from certain insects (as cochineal) and molluscs, and a number of mineral colors. In 1856, Perkin, in attempts to prepare quinine artificially, found that aniline (a coal-tar product) could be oxidized with chromic acid to yield a violet dye, to which was given the name "mauve." This was the first coal tar dye to be prepared, but since then no less than 3000 dyes derived from coal tar products have appeared on the market.

The dyes, then, may be either "natural" or "artificial." Among the former are logwood, fustic, Brazil wood, turmeric, natural indigo, etc., and they still find uses. The artificial dyes, however, play a much more important part in the industries. The ones of particular value are "fast" to light, rubbing and washing.

Dyes are also classified in accordance with their behavior towards fabrics as "substantive" or "direct" and "adjective" or "mordant" dyes. The "direct" dye can be applied directly (without a mordant) to the fabric, usually silk or wool. The "adjective" or "mordant" dye needs a "go-between"—a third substance which attaches itself to the fabric on the one hand, and the dye on the other; this third substance is the





WILLIAM HENRY PERKIN (1838-1907)  
PREPARED THE FIRST COAL-TAR DYE, "MAUVE" (P. 314), AND IS THEREFORE  
CALLED THE "FATHER" OF THE COAL TAR DYE INDUSTRY.

"mordant"—"bite into"—(e.g., various aluminium, chromium and iron salts, tannic acid, etc.). The combination of a mordant and a dye is known as a color "lake," the color of the "lake" varying with the type of mordant used. By using different mordants with the same dye, various colored lakes are produced. "Mordant" dyeing is mainly used for cotton goods. (In "direct" dyeing, the fabric is immersed directly in the prepared dye bath, heated to the required temperature, and agitated for a certain length of time.)

We cannot in this volume go into the various theories which have been suggested to explain the process of dyeing, beyond merely enumerating them: the chemical theory—a combination of the dye with the components of the fabric or certain constituents of the cell; the mechanical theory, based on adsorption; the solution theory, somewhat like the solution of one metal in another, as in an alloy; and the colloid theory, based on the colloidal properties of the reacting substances.

From the practical standpoint, the classification of dyes depends upon their behavior towards fibers.

The dyes are divided into:

(1) *Acid dyes*, which include nitro compounds and the sodium salts of sulfonic and carboxylic acids. These are direct dyes for wool and silk (in an acid bath), but are not adapted for the dyeing of cotton. The usual method employed here is to boil the material with the color solution in the presence of Glauber's salt and dilute sulfuric acid. (These dyes fade rapidly when the fabric is washed with soap or washing powders, but are resistant or "fast" to the effects of sunlight.)

(2) *Basic dyes*, substances which readily combine with acids to form salts. They are "direct" dyes for silk, artificial silk and wool, but not for cotton and linen. The last two have first to be "mordanted," the mordant used being acid in character (such as tannic acid, for example), since the dye itself is basic. Fabrics dyed with basic dyes fade when exposed to sunlight. The basic dyes owe their basic character to the presence of an amino group, and usually appear on the market as hydrochlorides, zinc double salts, compounds with oxalic acid, etc. The basic dyes were the first coal-tar colors, mauve itself (p. 314), being a basic dye.

(3) *Direct cotton dyes*, usually sodium salts of sulfonic and carboxylic acids and generally contain the azo ( $\text{—N=N—}$ ) grouping. They are adsorbed by the fiber directly and are used

mainly for dyeing cotton material (in the presence of NaCl or  $\text{Na}_2\text{SO}_4$ ).

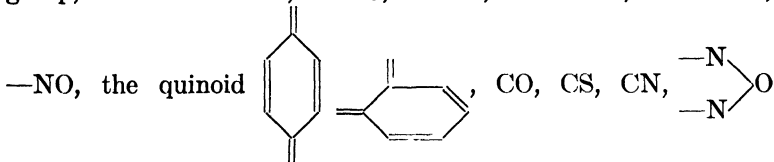
(4) *Sulfur dyes*—produced from various aromatic organic compounds by the action of sulfur and sodium sulfide. They are used for dyeing cotton and are fairly “fast” to washing.

(5) *Vat dyes*. These dyes are first reduced (generally with sodium hyposulfite, usually called sodium hydrosulfite,  $\text{Na}_2\text{S}_2\text{O}_4$ ), the fabric being then agitated in the reduced dye bath and exposed to the air (whereby the dye is oxidized). Examples of such dyes are indigo and anthraquinone dyes. They are very stable, being the “fastest” colors known.

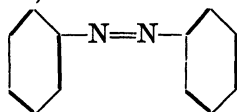
(6) *Mordant dyes*, which are generally of a phenolic or acidic character. Here mordants must be used to fix the dye to the fabric. Examples of mordant dyes are the coloring matters of dye woods (such as logwood and fustic) and alizarin.

(7) *Ingrain dyes*. These include substances (such as aniline black and para red) which are really only formed in the dye bath as a result of the chemical combination of two or more compounds. They are mainly cotton dyes.

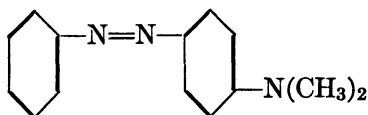
The classification just described is a somewhat empirical one and arose in response to the practical needs of the dyer. There is still another classification, a more scientific one, based on the presence of certain groups in the molecule of the dyestuff. All dyes, in the first place, contain a **chromophore**, or color-producing group, such as the nitro,  $-\text{NO}_2$ , the azo,  $-\text{N}=\text{N}-$ , the nitroso,



(azoxy) groups, etc. But before the colored body can become a dye, it must also possess either acidic or basic characteristics, so that it can attach itself to the fiber, or to the tissue (within the cell). These acidic or basic properties are given to the dye when **auxochrome** groups are present, such as  $\text{OH}$ ,  $\text{SH}$ ,  $\text{NH}_2$ ,  $\text{NHR}$ ,  $\text{NR}_2$ , etc. For example, azobenzene,



which is a colored compound, is not a dye, but *p*-dimethylamino-azobenzene,

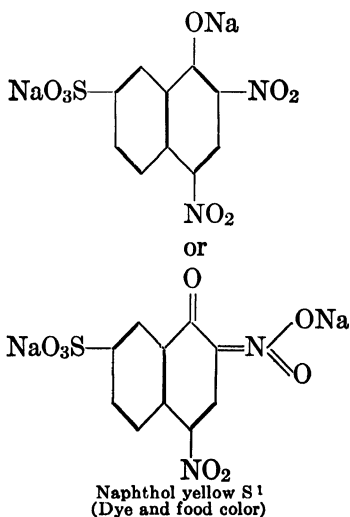


is a dye.

The entire subject of dyes is so extensive, that nothing more than a few members of the class can be mentioned here. However, the latest, and generally accepted classification of dyes will be given, and each type will be illustrated by one or more examples of dyes, stains or indicators in use. (The student should make a point here of noting the presence of chromophore and auxochrome groups in these compounds.)

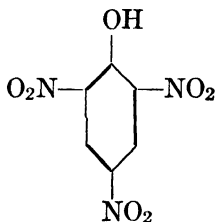
CLASSES OF DYESTUFFS	EXAMPLES
Nitroso dyes	<p>Resorcin green (Dye)</p>

Nitro dyes



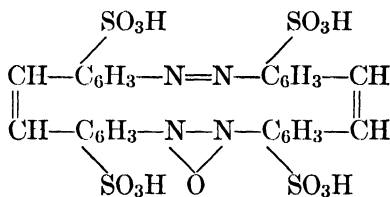
CLASSES OF  
DYESTUFFS

## EXAMPLES



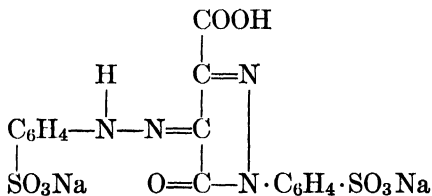
Picric acid  
(Dye and explosive)

## Stilbene dye



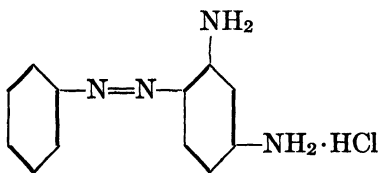
Sun yellow <sup>1</sup>  
(Dye)

## Pyrazolone dyes



Tartrazin <sup>1</sup>  
(Dye, stain and food color)

## Azo dyes

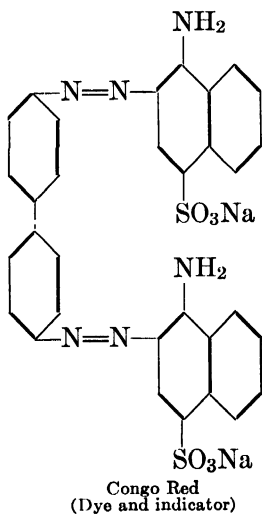
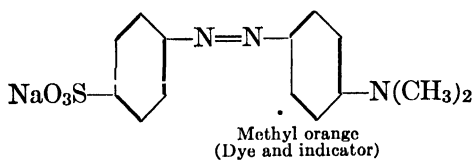
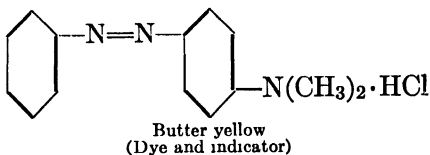


Chrysoidine  
(Dye)

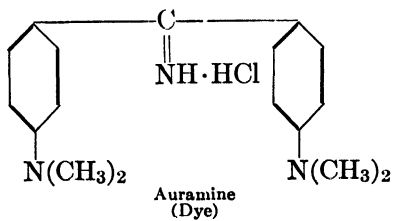
<sup>1</sup> Notice the presence of the sulfonic acid grouping, or of its salt, as part of the structure of some of these dyes. The presence of this group increases the solubility of the dye in water.

CLASSES OF  
DYESTUFFS

## EXAMPLES



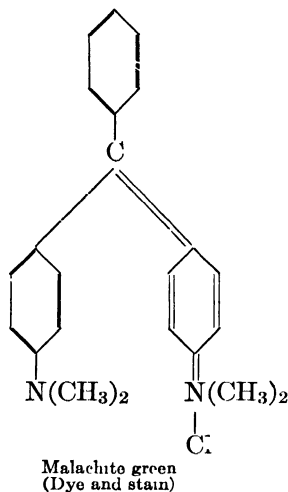
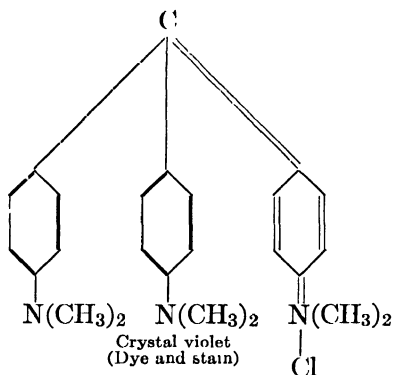
## Diphenylmethane dyes



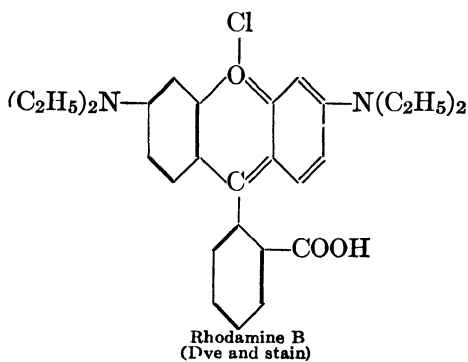
CLASSES OF  
DYESTUFFS

## EXAMPLES

## Triphenylmethane dyes



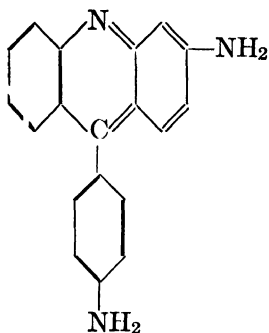
## Xanthene dyes



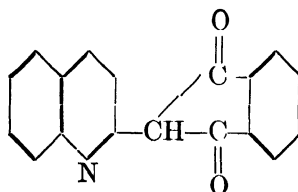
CLASSES OF  
DYESTUFFS

## EXAMPLES

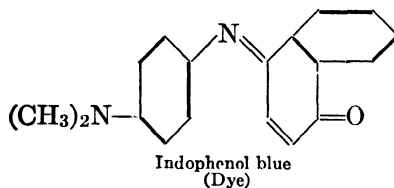
## Acridine dyes

Chrysaniline  
(Dye)

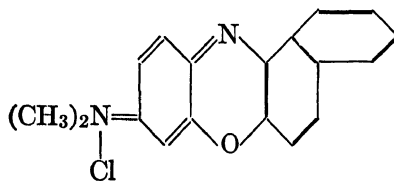
## Quinoline dyes

Quinoline yellow  
(Dye)

## Indophenol dyes

Indophenol blue  
(Dye)

## Oxazine dyes

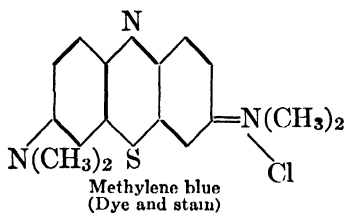
Meldola's blue  
(Dye)



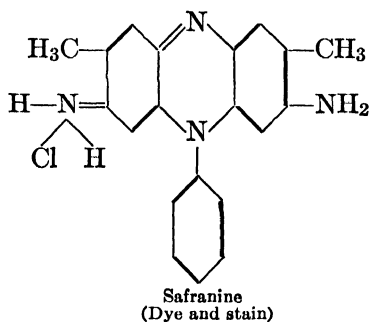
CLASSES OF  
DYESTUFFS

## EXAMPLES

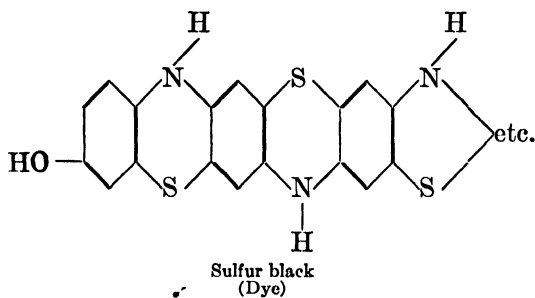
## Thiazine dyes



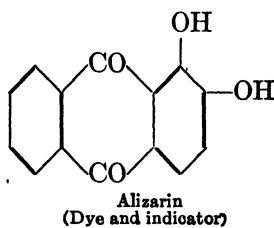
## Azine dyes



## Sulfur dyes

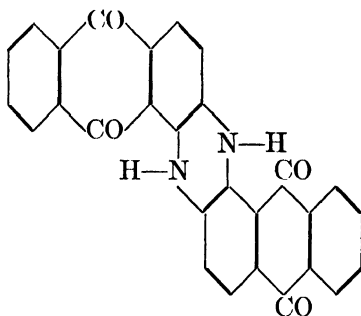


## Anthraquinone dyes

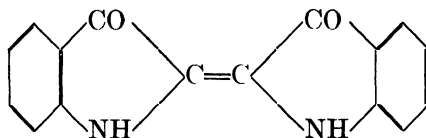


CLASSES OF  
DYESTUFFS

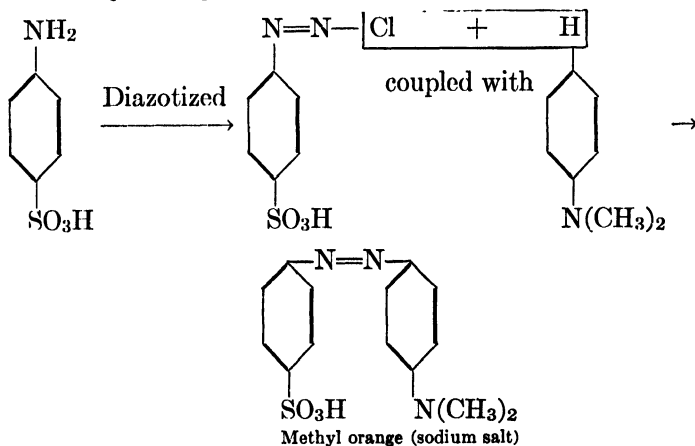
## EXAMPLES

Indanthrene blue R  
(Dye)

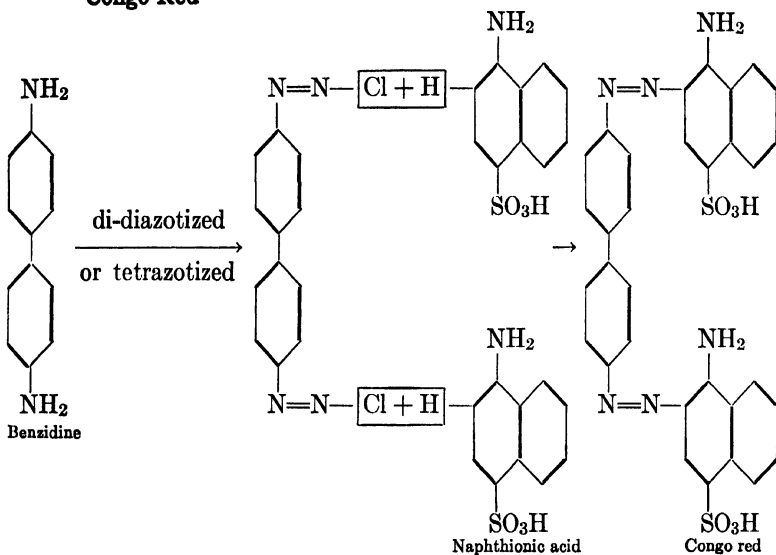
## Indigo dyes

Indigo  
(Dye)

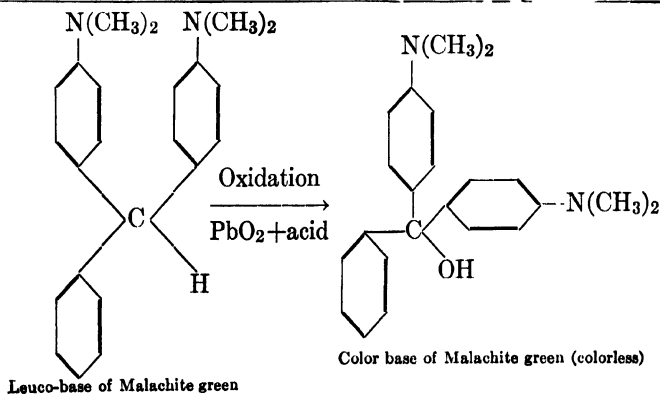
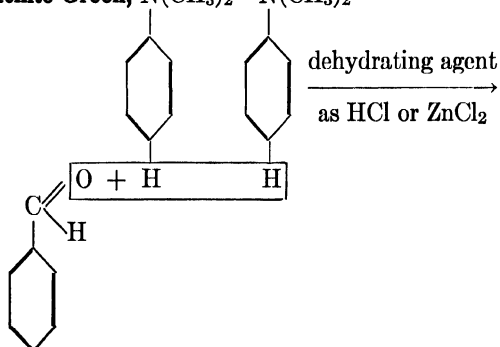
While the preparation of all of the above dyes cannot be given here, the principles employed in the synthesis of a few of them will be included.

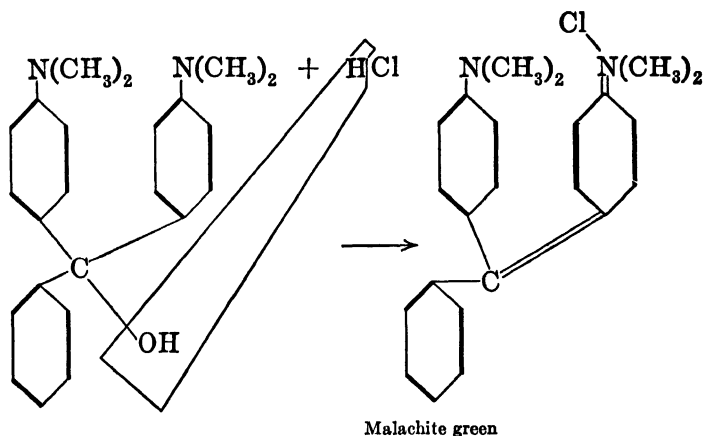
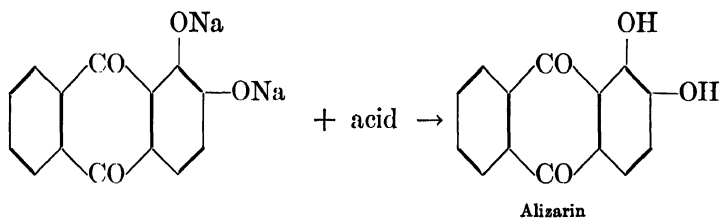
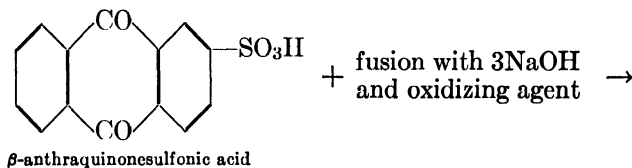
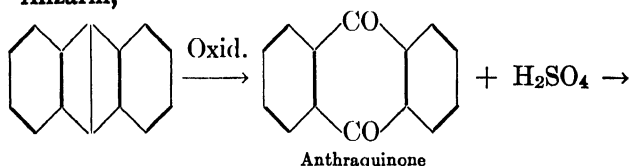
**Methyl Orange**

**Congo Red**



**Malachite Green,  $\text{N}(\text{CH}_3)_2$**



**Alizarin,**

(The preparation of phenolphthalein is given on p 274 and of indigo on p. 309).

**STAINS**

Dyes have come into use in bacteriology, because very often various bacteria can be differentiated by "staining" them with dyes. A stain is a dye or any other substance which colors tissues so that they can be submitted to microscopic examination.

Basic aniline dyes are the type of stains commonly used; these show special affinity for the nuclei of cells. Acid dyes are also sometimes used; these usually have a selective affinity for the protoplasm. Some of the most commonly employed aniline dyes are methylene blue, gentian violet, fuchsin, crystal violet, safranine, etc.

The chemistry of the process involved in staining is probably not unlike that which occurs in dyeing; there may be a chemical combination between the dye and the protoplasm of the cell, or a process of adsorption may be involved, or possibly both processes are operative.

(Recent research has resulted in the production of a "tripan-red" type of dye, of unpublished composition, known as "Bayer 205," which appears to be the most active trypanocide yet discovered. It has been used with success in advanced cases of African sleeping sickness.)

# READING REFERENCES

TILDEN—Chemical Discovery and Invention in the Twentieth Century (1916), chap. 21 (Production of Dyes); chap. 30 (Natural Colors).

WOOD—Chemistry of Dyeing.

RAMSEY AND WESTON—Artificial Dyestuffs.

PERKIN AND EVEREST—The Natural Organic Coloring Matters.

ROGERS—Manual of Industrial Chemistry. (1931), p. 1255 (Dyestuffs and Their Applications).

WATSON—Color in Relation to Chemical Constitution.

HARROW—Eminent Chemists of Our Times. (1927), (Perkin and Coal-tar Dyes).

HERTY—American Progress in Dye Manufacture. *Journal of Industrial and Engineering Chemistry*, **16**, 1021 (1924).

CONN—Biological Stains.

ROSE—Growth of the Dyestuffs Industry. *Journal of Chemical Education*, **3**, 973 (1926).

SHREVE—An Outline of the Dye Industry. *Journal of Chemical Education*, **3**, 1259 (1926).

ROWE—Colour Index.

FIESER—Discovery of Synthetic Alizarin. *Journal of Chemical Education*, **7**, 2609 (1930).

See p. 391 for list of books on Dyestuffs.

## CHAPTER XXXI

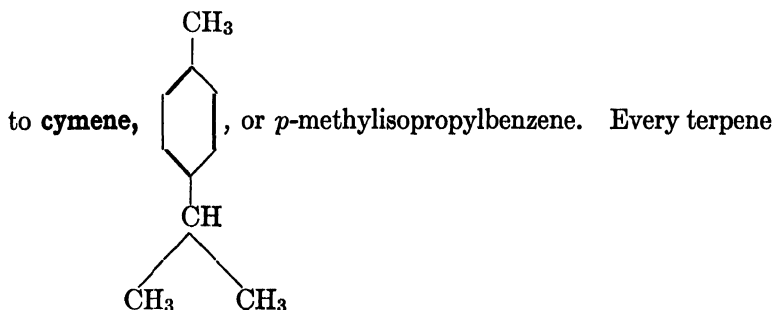
### TERPENES AND RELATED SUBSTANCES

THE terpenes are complex hydrocarbons, usually with the formula  $C_{10}H_{16}$ , present in, or obtained from, such substances as camphor, oil of turpentine and particularly "essential oils." ("Essential oils" are the products obtained when certain plants—such as the conifer and citrus—barks, leaves or flowers are distilled with steam; or when the oil is pressed or extracted with organic solvents. They are usually sweet-smelling substances containing a number of related organic compounds and are extensively used as flavors, in perfumery and in medicine.)

The compounds classified as terpenes fall into several classes:

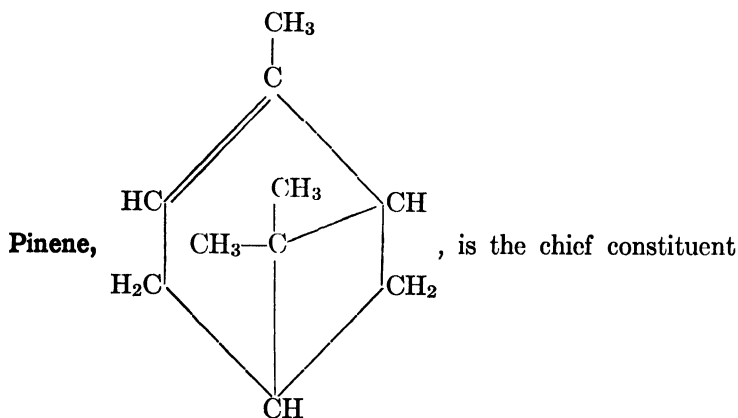
$C_5H_8$ —hemiterpenes,  
 $C_{10}H_{16}$ —terpenes (true terpenes),  
 $C_{15}H_{24}$ —sesquiterpenes,  
 $(C_{10}H_{16})_x$ —polyterpenes.

The terpenes are hydroaromatic hydrocarbons, closely related



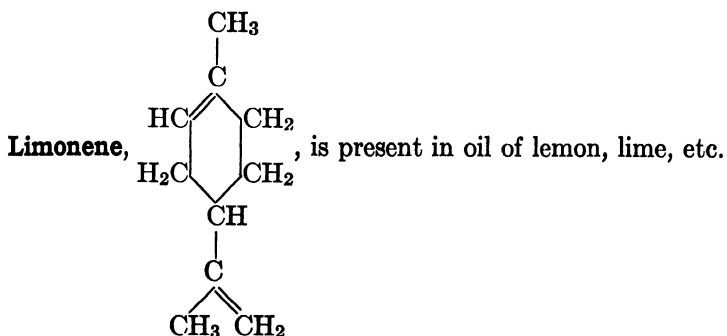
contains a hydrogenated benzene nucleus and either a methyl and isopropyl group, or radicals related to these groups.

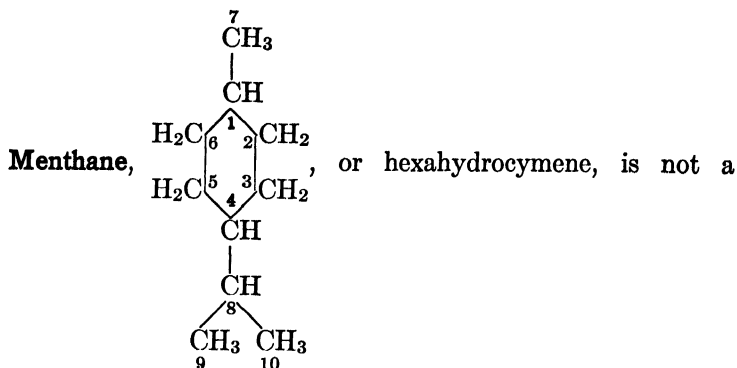
Some of the more important compounds belonging to the terpene group are as follows:



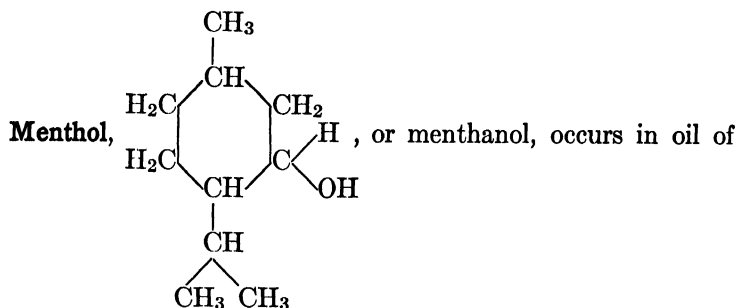
of oil of turpentine. Owing to the presence of a double bond, it forms addition products with halogens, halogen acids, nitrosyl chloride, nitrogen peroxide, etc. One such product, pinene hydrochloride (obtained by uniting pinene with hydrochloric acid), is "artificial camphor," which resembles camphor.

(When crude turpentine is distilled with steam, pure turpentine or "oil of turpentine" collects in the distillate and "rosin," or "colophony," a solid resin, remains in the still. The oil of turpentine is used in paints and varnishes and the rosin is used in soap making, varnishes, sealing wax, etc.)

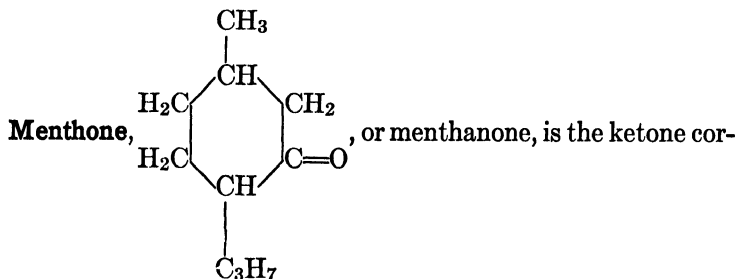




natural product, but we have a number of important substances related to it.

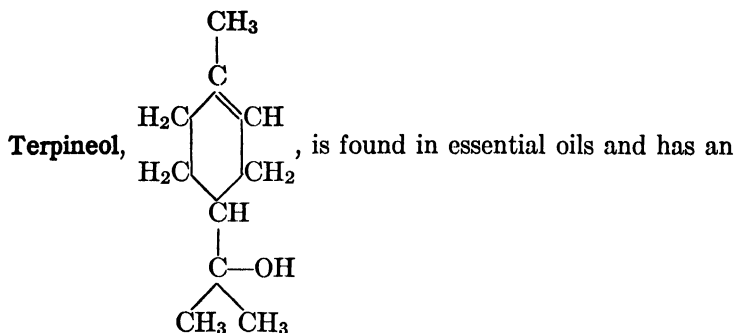


peppermint. It has a peppermint-like odor and finds extensive use as a flavoring agent.

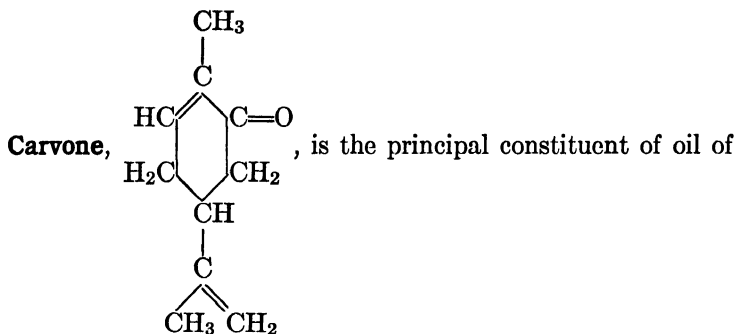


responding to menthane, and is also found in oil of peppermint. Like other ketones, it may be reduced to a secondary alcohol (in this case to menthol).

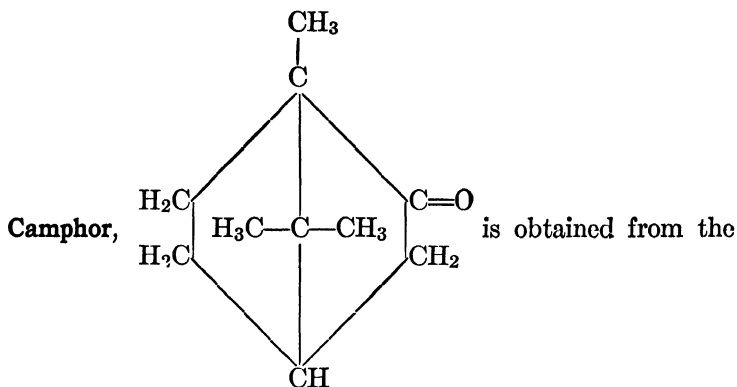




odor resembling that of lilacs.

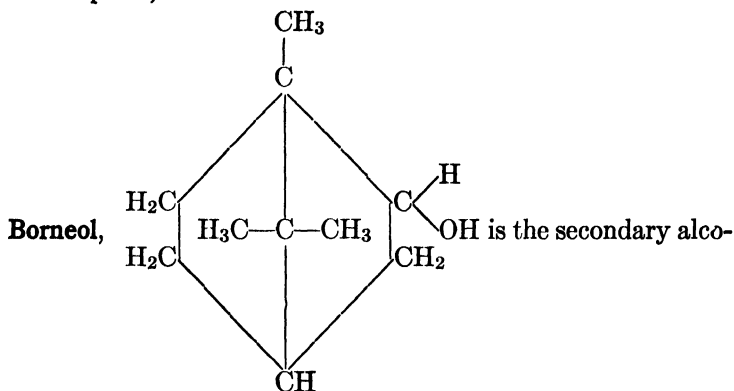


caraway and possesses the characteristic odor of this oil.



camphor tree by steam distillation. It may also be obtained synthetically from pinene hydrochloride (p. 329). It is largely used in the manufacture of celluloid (p. 184) and in pharmaceutical preparations. (The artificial camphors on the market are either pinene hydrochloride or triphenyl phosphate, p. 251. Artificial

camphor does not have the same structure as natural or synthetic camphor.)



hol obtained from camphor (a ketone) when the latter is reduced. It occurs in nature, being known as "Borneo-camphor," and has a camphor-like odor.

The following are the important olefin terpenes:

**Isoprene**,  $\text{CH}_2=\text{C}-\text{CH}=\text{CH}_2$ , or 2-methyl-1, 3-butadiene



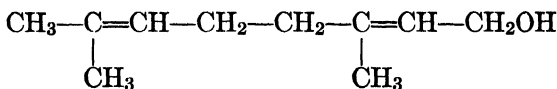
(see p. 38), is obtained by the distillation of rubber or caoutchouc.

**Citrene**,  $\text{CH}_3-\text{C}=\text{CH}-\text{CH}_2\cdot\text{CH}_2-\text{C}=\text{CH}-\text{CH}_3$ , is a ter-

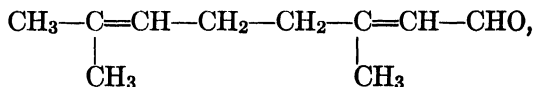


pene obtained from lemon oil.

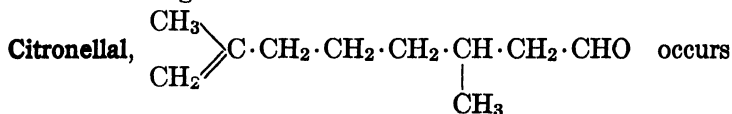
**Geraniol** (the alcohol),



is found in rose and geranium oils; and **citral** (the aldehyde),



in lemon and orange oils.



in oils of citrus fruits.

## TABLE OF ESSENTIAL OILS

Oil	Chief Known Constituents
Allspice	Eugenol; sesquiterpene
Angelica Root	Phellandrene; valeric acid
Angelica Seed	Phellandrene; valeric acid
Anise	Anethole; anisaldehyde
Birch	Methyl salicylate
Bitter Almond	Benzaldehyde; hydrocyanic acid; phenyloxyacetonitrile
Camphor	Camphor; borneol; pinene
Caraway	Carvone; <i>d</i> -limonene
Cedar Wood	Cedrene; cedar camphor
Celery Seed	Limonene; phenols
Cinnamon Bark	Cinnamaldehyde; eugenol
Citronella	Geraniol; citronellal
Clove	Eugenol
Cognac	Esters of caprylic acid
Eucalyptus	Phellandrene; cineol
Fennel	Anethole; fenchone
Garlic	Allyl propyl disulfide; diallyl disulfide
Geranium	Geraniol; citronellol
Ginger	Phellandrene
Guaiac Wood	Guaiacol
Hops	Humulene; geraniol; terpenes
Jasmine	Benzyl acetate; linalol
Juniper Berries	Pinene; cadinene; juniper camphor
Lavender	Linalyl acetate; linalol
Lemon	Limonene; phellandrene; citral; citronellol; geranyl acetate; linalol
Lime	<i>d</i> -Limonene; citral; methyl anthranilate
Mustard	Allyl isothiocyanate
Neroli	Linalyl acetate; linalol; geraniol; limonene
Nutmeg	Myristicin; pinene
Onion	Allyl propyl disulfide
Orange	Limonene
Pepper	Phellandrene; dipentene
Peppermint	Menthol; menthyl esters; menthone
Rose	Geraniol; citronellol; geranyl acetate
Sassafras	Safrol; eugenol; camphor; pinene; phellandrene
Spearmint	Carvone; limonene; pinene
Thyme	Thymol; carvacrol; cymene; linalol; borneol
Tolu	Esters of benzoic and cinnamic acids
Turpentine	Pinene

Valerian	Borneol; bornyl formate, acetate and isovalerianate; pinene; camphene
Wintergreen	Methyl salicylate
Ylang-ylang	Linalol; geraniol; benzoic esters; methyl ester of <i>p</i> -cresol.

(Oil of *Chenopodium*, an old household remedy for worms, is a mixture of various terpenes.)

### READING REFERENCES

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- DUNCAN—Some Chemical Problems of Today. (1911), chap. 7 (Camphor).
- DUNCAN—The Chemistry of Commerce. (1907), chap. 8 (Floral Perfumes).
- SLOSSON—Creative Chemistry. (1920), chap. 5 (Synthetic Perfumes and Flavors).
- GILDEMEISTER AND HOFFMANN—The Volatile Oils.
- ROGERS—Manual of Industrial Chemistry. (1931), p. 1049 (Essential Oils, Synthetic Perfumes and Flavoring Materials); p. 1090 (Resins, Gums and Turpentine).
- BOGERT—The Flower of the Organic Chemist: Perfumes Natural and Synthetic. *Journal of Industrial and Engineering Chemistry*, **14**, 359 (1922).
- POWER—The Distribution and Characters of Some of the Odorous Principles of Plants. *Journal of Industrial and Engineering Chemistry*, **11**, 344 (1919).
- ANON.—Turpentine. (Agricultural Bulletin 898.) Government Printing Office, Washington.
- CLARK—Applied Pharmacology. (1923), chap. 7 (Anthelmintics—Oil of *Chenopodium*, etc.).
- HOWE—Chemistry in Industry, Vol. I. (1924), chap. 16 (Perfumes and Flavors); chap. 20 (Chemistry in the Rubber Industry).

## CHAPTER XXXII

### VEGETABLE ALKALOIDS

VEGETABLE alkaloids are basic nitrogenous substances which occur in plants usually in combination with organic acids (citric, tartaric, oxalic, malic, etc.) and which are characterized by powerful physiological activity. They contain the elements C, H, N or C, H, O and N and are complex in constitution, generally containing pyrrole, pyrrolidine, pyridine, quinoline or isoquinoline groups in their structure. Only a very brief presentation of the subject can be given here.

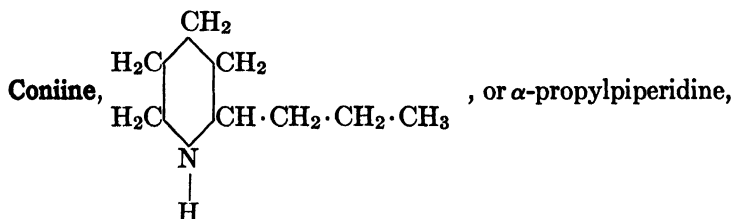
Alkaloids occur in dicotyledonous plants. Most of them are crystalline (coniine and nicotine are liquids) and most of them are levorotatory. They are insoluble in water, soluble in alcohol, ether, chloroform, etc., to a greater or less extent, form water-soluble salts with acids, have a bitter taste and some are excessively poisonous. Most of the alkaloids are used in the form of salts, such as hydrochloride, nitrate, bisulfate, sulfate, phosphate, etc.

The following substances, known as "alkaloidal reagents," precipitate alkaloids from their aqueous or acid solutions; tannic acid, potassium-mercuric iodide ( $KI + HgI_2$ ), phosphomolybdic acid, picric acid and phosphotungstic acid. (The "alkaloidal reagents" are quite often used to precipitate proteins.)

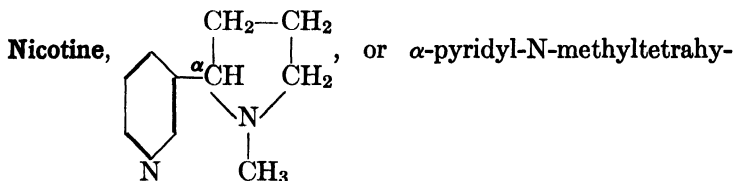
Color reactions are frequently used to identify certain alkaloids.

The method of extraction from plants often consists in extracting with acidified ( $HCl$  or  $H_2SO_4$ ) water and reprecipitating with bases.

The number of alkaloids known is very large; only a few of the more important ones can be mentioned here.



is obtained from the seeds of spotted hemlock and has been produced synthetically. It is very poisonous, has a disagreeable odor and an acrid taste. (Chemically, it is the simplest alkaloid.)



dropyrrole, is present in tobacco leaves and is used as an insecticide.

**Piperine**,  $C_{17}H_{19}NO_3$ , occurs in pepper, from which it is extracted.

**Atropine**,  $C_{17}H_{23}NO_3$ , obtained from the *Deadly Nightshade* (belladonna), is used as a mydriatic (dilating the pupil) in ophthalmic surgery.

**Homatropine**, an artificial alkaloid derived from atropine, dilates the pupil more rapidly than atropine and the effect is not as lasting.

**Cocaine**,  $C_{17}H_{21}NO_4$ , is contained in coca-leaves. It is used as a local anesthetic in minor operations, though, owing to its extreme toxic properties, it has been largely replaced by novocaine, butyn, etc. (p. 290).

**Quinine**,  $C_{20}H_{24}N_2O_2$ , is obtained from cinchona bark, etc. It is used in the treatment of malaria, as a "bitter" (to increase appetite), to reduce fever, etc.

**Cinchonine**,  $C_{19}H_{22}N_2O$ , from cinchona bark, resembles quinine in its physiological properties, though its effects are not so pronounced.

**Strychnine**,  $C_{21}H_{22}N_2O_2$ , and **brucine**,  $C_{23}H_{26}N_2O_4$ , occur together in the seeds of nux vomica and in *St. Ignatius'* beans. Strychnine is an extremely poisonous substance, acting on the spinal cord and producing characteristic convulsions. In very

small doses, it is used as a tonic, to increase the appetite, as a heart stimulant and in various forms of paralysis. Brucine acts similarly.

**Morphine**,  $C_{17}H_{19}NO_3$ , is the chief alkaloid of opium (which is the dried juice of the seed capsules of a variety of poppy). It is used as an analgesic and as a soporific.

**Heroin** is a diacetyl derivative of morphine. Its effects are, in general, similar to those of morphine. It is used as a sedative and to lessen coughing.

**Narcotine**,  $C_{22}H_{23}NO_7$ , and **codeine**,  $C_{18}H_{21}NO_3$ , are also present in opium and are closely related to morphine.

**Dionine** is an artificial alkaloid made from morphine (ethyl morphine) and is used to produce sleep and relieve pain.

**Pilocarpine** is the active principle obtained from the leaves of *Pilocarpus jaborandi*, a Brazilian shrub. It is used principally to increase perspiration.

**Emetine**, the active alkaloid of ipecac, is used in the treatment of amoebic dysentery (because of its destructive action on amoebae) and also in the treatment of pyorrhoea alveolaris, an infected condition of the teeth sockets.

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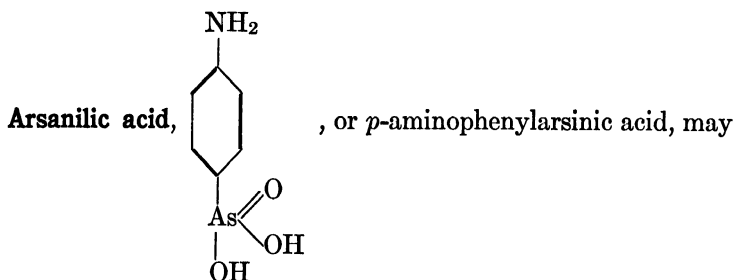
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## CHAPTER XXXIII

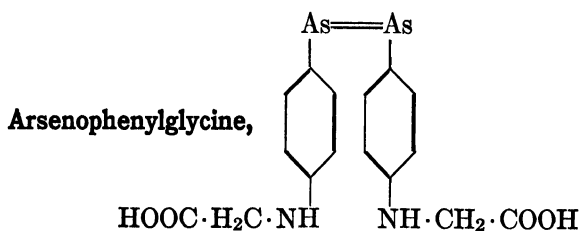
### ARSENIC AND MERCURY COMPOUNDS OF THE AROMATIC SERIES

ARSENIC and mercury compounds, particularly the former, have found wide application in the treatment of diseases caused by protozoa (such as in syphilis). The organic combinations of these metals have an advantage over the inorganic compounds in that they are less toxic to mammals and more toxic to protozoan parasites.

#### ARSENIC COMPOUNDS

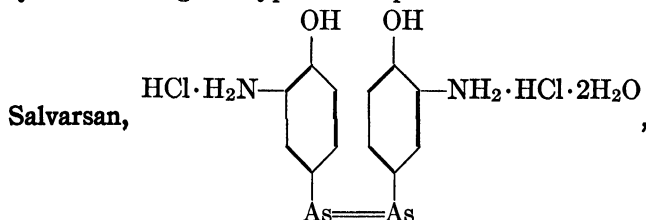


be regarded as being derived from arsenic acid,  $\text{AsO}(\text{OH})_3$ , in which one OH group is replaced by aniline, and is prepared by combining aniline with arsenic acid. The monosodium salt is known as "atoxyl" and "soamin" and, though used at one time in the treatment of syphilis, relapsing fever, etc., it is now chiefly of interest as an intermediate in the preparation of salvarsan.

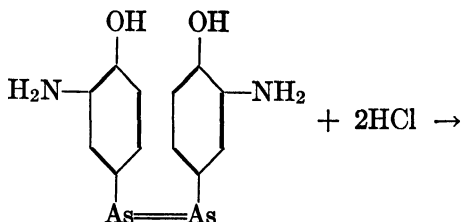
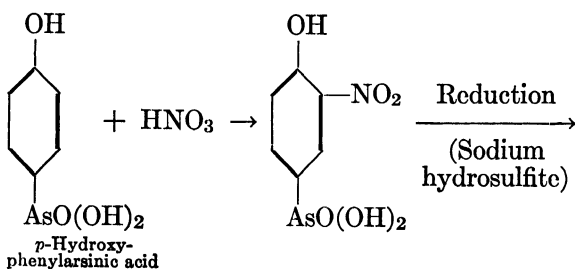
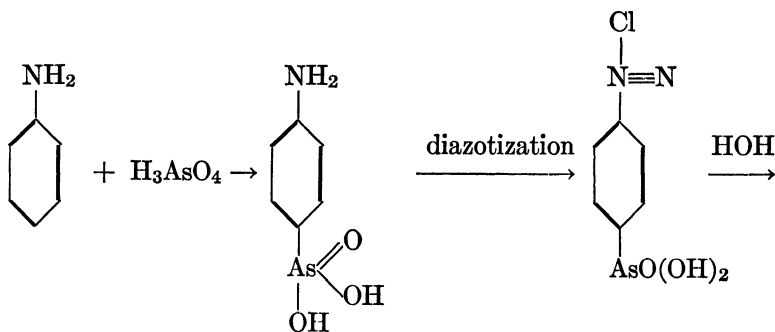


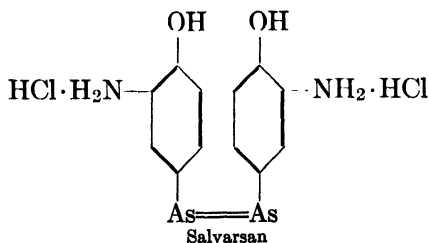


was introduced by Ehrlich as a substance even less toxic than atoxyl and of a higher trypanocidal power.



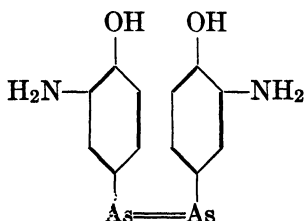
or 3,3'-diamino-4,4'-dihydroxyarsenobenzene dihydrochloride, known also as arsphenamine and "606," was first synthesized by Ehrlich and introduced by him for the treatment of syphilis. One method of preparing it is as follows:



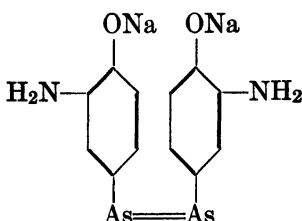


While we cannot, in this book, enter into a prolonged discussion regarding the interesting question of the effect of chemical structure upon physiological action, Ehrlich's discovery of salvarsan deserves a few words of comment. When Ehrlich first began his celebrated research, he was aware of the fact that trypanosomes—a group of parasites—are killed by a number of dyes and a number of organic arsenic compounds, of which “atoxyl” was the most important. This compound contains pentavalent arsenic. The important discovery was made that although it would cure animals of trypanosomiasis, it had no toxic action upon trypanosomes *in vitro*. After many trials with many arsenical compounds, Ehrlich was in a position to formulate this general rule: that only compounds containing trivalent arsenic were effective in killing trypanosomes, and that the effectiveness of compounds containing pentavalent arsenic depended upon their reduction in the body to the trivalent form. The most efficient substances were found to be compounds containing trivalent arsenic joined to a benzene ring and containing also an amino group. This was later still further improved upon by the discovery that the most effective compounds were those containing an OH group in the *p*-position, an amino group, and arsenic—as in salvarsan itself.

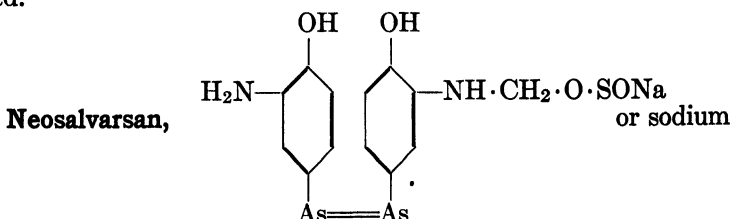
Salvarsan, that is the dihydrochloride salt, is soluble, but it forms an acid solution, and is irritant and toxic. By the addition of two gram molecules of NaOH to one of salvarsan, the neutral base is obtained:



This is insoluble. Upon the further addition of two gram molecules of NaOH, the sodium salt is produced:



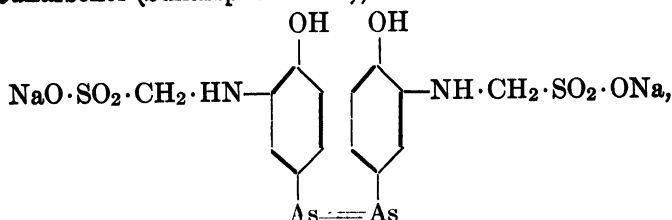
and this is soluble in water. It is the form of salvarsan generally used.



3,3'-diamino-4,4'-dihydroxyarsenobenzene - *N* -methylenesulfinate, is also known as neoarsphenamine or "914" and was introduced by Ehrlich because of its greater solubility than salvarsan. It is prepared by combining salvarsan with sodium formaldehyde sulfoxylate ( $\text{HOCH}_2 \cdot \text{OSONa}$ ).

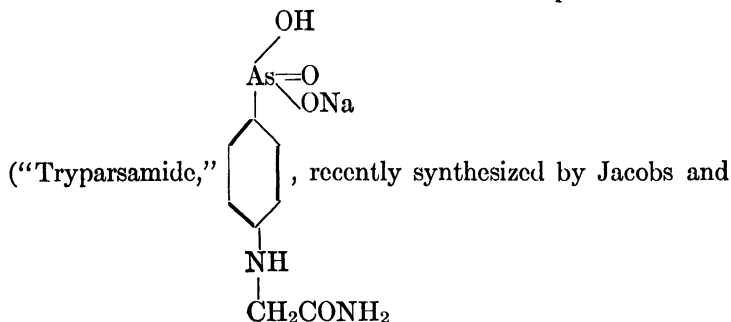
Silver salvarsan and silver neosalvarsan have the same uses as salvarsan, but it is claimed that the presence of silver in the molecule raises the toxicity to parasites without increasing the toxicity to mammals. "Luargol," which contains antimony in addition to silver and arsenic, is another salvarsan derivative for which therapeutic claims have been made. "Galyl" is a salvarsan derivative containing phosphorus in addition to arsenic.

**Sulfarsenol (Sulfarsphenamine),**



or disodium 3,3' - diamino - 4,4' - dihydroxyarsenobenzene - *N* - di-

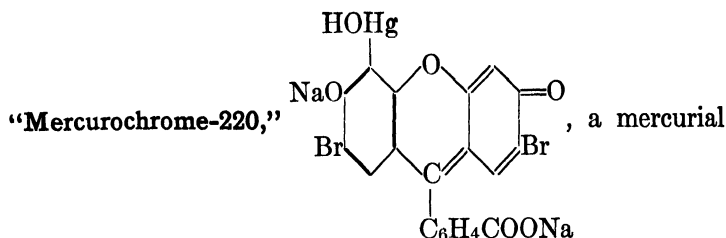
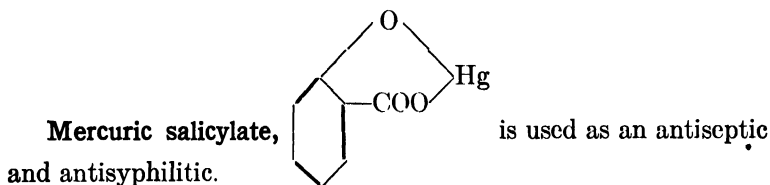
methylensulfonate, is similar in its uses to neosalvarsan, but it is claimed that its solutions are more stable in the presence of air.



Heidelberger, has been successfully applied in the treatment of human sleeping sickness.)

$(\text{C}_6\text{H}_5)_2\text{As}\cdot\text{Cl}$ , diphenylchloroarsine, was used as a "sneeze" gas in the war.

### MERCURY COMPOUNDS



derivative of fluorescein, has recently been introduced as a very active germicide and is gradually replacing tincture of iodine used for that purpose.

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## CHAPTER XXXIV

### A BRIEF OUTLINE FOR THE IDENTIFICATION OF ORGANIC COMPOUNDS

THE identification of an organic compound is not a simple matter. We have no methods quite as clearly defined as those of inorganic chemistry.

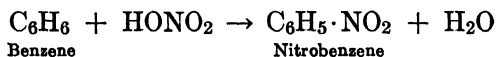
In the identification of an organic compound, the first step is to make certain that the compound is in a pure state—a fact which may very often be determined by ascertaining the boiling point or melting point, or by associating the compound with some other physical constant, such as specific gravity, etc.

In the next place, an elementary analysis should clearly indicate the elements present in that compound. Once this is determined, certain limits are immediately set as to the kind of compound it can be. For example, a compound which upon analysis shows the elements C, H and O only, cannot be an amine.

The classification of organic compounds and many of their most characteristic reactions are intimately bound up with the presence, within the molecules of these compounds, of various "groups," such as OH, NH<sub>2</sub>, COOH, etc. In this chapter the attempt will be made to give a brief résumé of some of the reactions used for identifying such groups. Incidentally, this chapter ought to serve, to some extent, as a review.

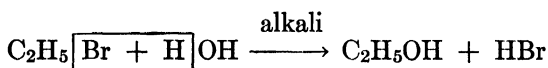
**Hydrocarbons.**—Usually, these are colorless gases, liquids or solids, insoluble in water and soluble in alcohol and ether. (Where tests reveal that no elements other than carbon and hydrogen are present, the indications would immediately point to the presence of a hydrocarbon.) The paraffin hydrocarbons are very inert substances. The olefins add two bromine atoms to form saturated compounds, and the acetylenes generally respond to the

formation of metallic acetylides. The aromatic hydrocarbons may, as a rule, be nitrated, to form nitro derivatives:



Where the aromatic compounds contain a side-chain (as a  $\text{CH}_3$  group, for example), this can be oxidized (by chromic acid or potassium permanganate or dilute nitric acid) to the carboxyl group. The hydrocarbons with condensed benzene nuclei (such as naphthalene, anthracene, etc.) are solids and may be identified by their oxidation products and, very often, by the fact that they form well-defined picrates (with picric acid) with definite melting points. The terpene hydrocarbons (such as pinene) present many difficulties when attempts are made to isolate them. Sometimes a number of physical properties (boiling point, density, specific rotation, etc.) prove helpful.

**Halogen compounds.**—The aliphatic compounds are almost non-ionizable and practically insoluble in water. The alkyl chlorides are lighter than water while the bromides and iodides are heavier. They are hydrolyzed to the corresponding alcohols; e.g.,



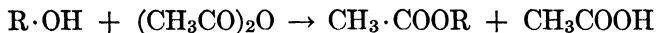
With the aromatic halides, where the halogen is attached to the benzene nucleus, we get substances which are either liquids or solids, with a faint, agreeable odor, and insoluble in water. They are stable compounds and do not, for example, react with potassium hydroxide. They are utilized in the *Fittig* synthesis. The aromatic halogen compounds, with the halogen in the side-chain, behave similarly to the aliphatic halogen compounds and possess lachrymatory properties.

**Alcohols.**—As a rule, the monohydroxy alcohols are colorless liquids, neutral in reaction and some of them have a characteristic odor and taste. The solubility in water decreases with increasing molecular weight. The polyatomic alcohols are oily liquids or crystalline solids, soluble in water, and less soluble, or altogether insoluble in ether.

Primary alcohols when oxidized (with chromic acid, for example), give first an aldehyde and then an acid; secondary alcohols yield ketones; and tertiary alcohols break down into

carboxylic acids containing fewer carbon atoms than the original compound.

The OH group is very often identified by forming esters, either with acetyl chloride or acetic anhydride; e.g.,



Many of these esters have characteristic odors and by submitting them to a quantitative hydrolysis, it becomes possible to determine whether the original compound contains one or more OH groups. (For every OH group, one acetyl group is used.)

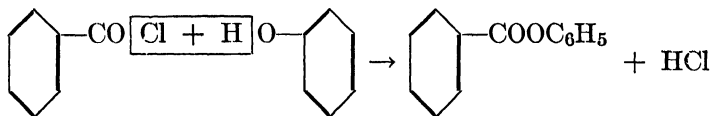
**Phenols.**—These are usually crystalline solids. (The solubility in water increasing with the number of OH groups present in the ring.) They are weak acids, being dissolved in alkalis forming salts.

Nearly all phenols give a precipitate of a polybromophenol when treated with bromine water; e.g.,



and yield deeply colored solutions with ferric chloride. Many give the *Liebermann* test (a deep blue or green color, when the phenol is dissolved in cold conc.  $H_2SO_4$ , and a little  $NaNO_2$  added). (This test is also used for identifying the nitroso group.)

Phenols, like alcohols, combine with acetic anhydride to form esters; they also form esters with acyl chlorides and these can be identified by their melting or boiling points; e.g.,



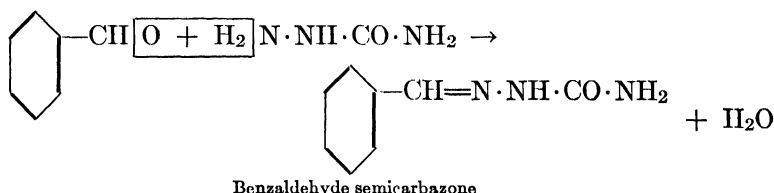
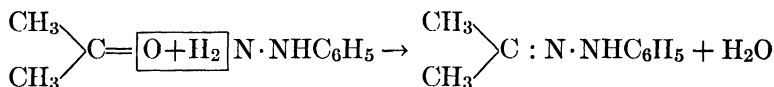
**Ethers.**—These are neutral, chemically inactive liquids. They are often identified by their boiling points, or by the following reaction:



**Aldehydes and Ketones.**—The lower aldehydes are liquids possessing a characteristic odor, and, unlike ketones, reduce *Fehling's* or ammoniacal silver nitrate solution. For purposes of identification, aldehydes and ketones may be combined with hydroxylamine to form oximes, with phenylhydrazine to form phenyl-



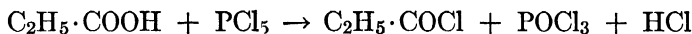
hydrazones, and with semicarbazide (aminourea) to form semicarbazone; e.g.,



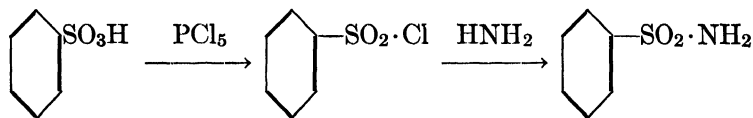
Most aldehydes give the *Schiff* test (restoring the pink color to a solution of magenta which has been decolorized with  $\text{SO}_2$ ).

**Carboxylic acids.**—The lower aliphatic monobasic acids (as formic and acetic) are liquids, soluble in water, but the solubility decreases with increasing molecular weight. The higher members (like palmitic and stearic) are solids, insoluble in water. The aliphatic polybasic acids (like oxalic and succinic) are solids, soluble in water. Many of the aromatic acids (like benzoic and *o*-toluic) are not very soluble in cold, but more so in hot water.

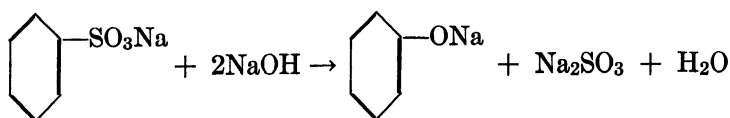
The acidity of the substance may be determined by titrating with standard alkali. The conversion of the acid to the corresponding ester (with alcohol and a dehydrating agent) and the elimination of the carboxyl group (in the form of  $\text{CO}_2$ ) by heating with soda lime, are often of help in identifying the acid. Often the acid is converted to its acyl halide; e.g.,



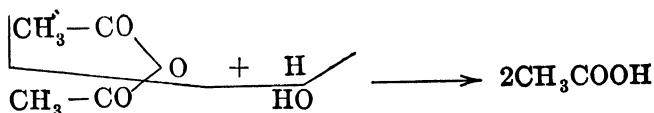
**Aromatic sulfonic acids.**—As a rule, these are soluble substances, difficult to crystallize. For purposes of identification, the corresponding amide is prepared by first forming the sulfonyl chloride with  $\text{PCl}_5$  and then converting the latter to the amide—with definite m.p.—:



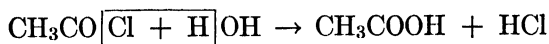
Fusion with alkali to form the corresponding phenol is also sometimes employed:



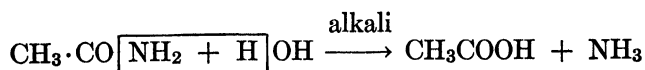
**Acid anhydrides.**—As a rule, the aliphatic compounds are colorless liquids, insoluble in water and soluble in alcohol and ether. The aromatic compounds are solid. They are usually identified by hydrolyzing them to the corresponding acids or salts; e.g.,



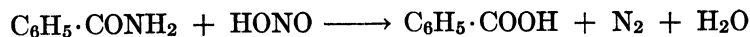
**Acyl halides.**—These are pungent-smelling liquids, easily convertible (hydrolysis) into the corresponding acids; e.g.,



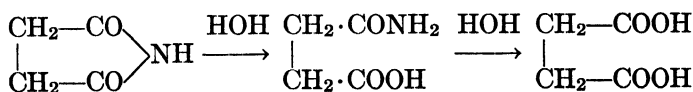
**Acid amides.**—These are, as a rule, well defined, crystalline substances. They can be hydrolyzed with boiling alkali to the corresponding acids (salts); e.g.,



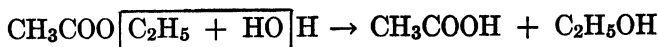
or



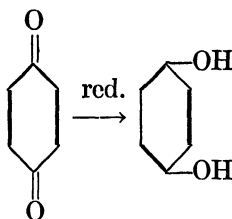
**Acid imides**, like the amides, are hydrolyzed by boiling with alkalies:



**Esters.**—These are volatile compounds, insoluble in water, with agreeable odors. The esters may be hydrolyzed with alkali; e.g.,

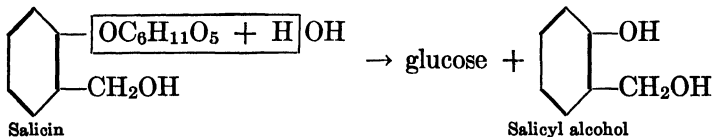


**Quinones.**—These are colored compounds (yellow or red). The *p*-benzoquinone is volatile with steam. As a rule, they can be reduced;



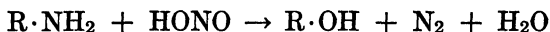
**Carbohydrates.** These are solids soluble in water (except the polysaccharides, such as starch, etc.). Among the polysaccharides, starch gives a blue color with iodine, and glycogen and the dextrans, a violet to a violet-red. The sugars (lactose, maltose, galactose, levulose, glucose) reduce *Fehling's* solution and form osazones with phenylhydrazine. Sucrose or cane sugar is a notable exception. They are optically active.

**Glucosides.**—On hydrolysis, these yield glucose, in addition to one or more substances; e.g.,

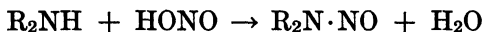


**Amines.**—The lower members of the aliphatic amines (like methylamine) are flammable gases, with an odor resembling ammonia; the higher members (like butylamine) are liquids. With acids they form salts, soluble in water and in alcohol. The aromatic amines are either liquids (like aniline) or solids (like diphenylamine).

With aliphatic amines, nitrous acid converts the primary amine into the corresponding alcohol:



the secondary amine is converted into the yellow nitrosoamine:

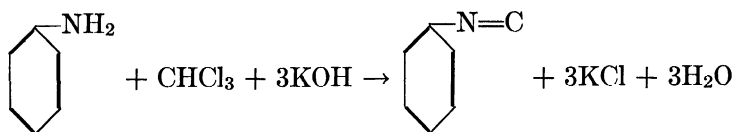


and the tertiary amine is not acted upon.

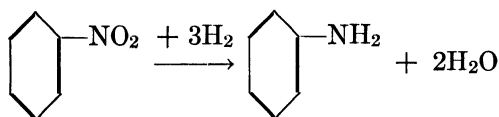
With the aromatic amines, the manner in which nitrous acid behaves will be dependent upon whether the  $\text{NH}_2$  group is in the nucleus or in the side-chain. If the amino group is in the nucleus,

diazonium salts are formed (in the cold) which are converted to phenols on heating; if the  $\text{NH}_2$  group is in the side-chain, then the compound behaves like an aliphatic amine. With secondary aromatic amines, nitrous acid yields nitroso derivatives similar to those obtained with aliphatic secondary amines. A tertiary amine such as dimethylaniline reacts with  $\text{HONO}$  to produce *p*-nitrosodimethylaniline.

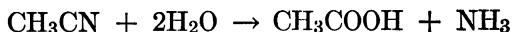
The primary amines, whether aromatic or aliphatic, give the carbylamine reaction (the isocyanide is formed which has a disgusting odor); e.g.,



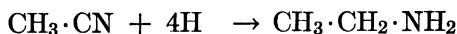
**Nitro compounds.**—Only the aromatic nitro compounds are of importance. Usually, these are oily liquids or solids, insoluble in water and dilute  $\text{HCl}$ . They are identified by being reduced to the corresponding amines; e.g.,



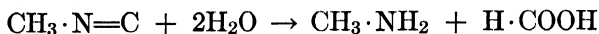
**Cyanides and Isocyanides.**—The cyanides are liquids or solids with an agreeable odor. They are hydrolyzed to the corresponding acids; e.g.,



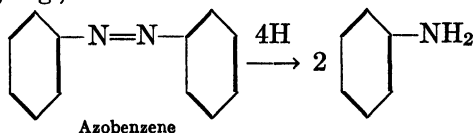
and are reduced to the primary amines; e.g.,



The isocyanides or carbylamines possess a disgusting odor. On hydrolysis, they yield formic acid and an amine; e.g.



**Azo compounds.**—These are colored solids and include a large class of important dyes. They yield, on reduction, amino compounds; e.g.,



**Purines**, of which uric acid and caffeine are examples, are not easily identified. Most of them give the *murexide* test (evaporate the substance on a water bath to dryness with conc.  $\text{HNO}_3$ , cool and make alkaline with ammonia or  $\text{NaOH}$ ; a violet or red color is produced).

**Alkaloids**.—These are mostly solids (nicotine, and coniine are exceptions), soluble in alcohol, somewhat less soluble in ether, chloroform and benzene, and usually insoluble in water. Most of them are levorotatory. They dissolve in acids, forming salts, and are reprecipitated by alkalies. Alkaloids are not easily identified, but as a class they are precipitated by the “alkaloidal reagents,” such as tungstic, phosphomolybdic, tannic and picric acids, potassium-mercuric iodide, etc. Many of them are identified by color reactions with  $\text{H}_2\text{SO}_4$  and an oxidizing agent.

**Sulfur compounds**.—The sulfonic acids have already been treated. The only others that need be mentioned here are the mercaptans (e.g.,  $\text{C}_2\text{H}_5\text{SH}$ ) and the sulfides (e.g.,  $(\text{C}_2\text{H}_5)_2\text{S}$ ). Both types of compounds have very disagreeable odors.

**Terpenes and allied compounds**.—These substances are flammable, mostly volatile, possess characteristic odors and are insoluble in water, but soluble in many organic solvents. They do not belong to the aliphatic or to the aromatic series of compounds and are, as a rule, complex in structure. Certain derivatives are usually prepared in order to identify them.

**Proteins**.—These are complex substances consisting, in the main, of linkages of amino acids. They are identified by a number of color tests. With the *Millon's* reagent (mercuric nitrate containing nitrous acid) most of them give a red color or precipitate. When heated with  $\text{HNO}_3$  a yellow color is developed and this is changed to an orange on the addition of ammonia (*xanthoproteic* reaction). When mixed with a strong solution of  $\text{KOH}$  and a drop or two of  $\text{CuSO}_4$  is added, a violet color is obtained (biuret reaction).

### General Solubilities of Classes of Organic Compounds

**General Rule**.—A solvent dissolves those compounds which are chemically closely allied to it.

Hydrocarbons and their halogen substitution products are either insoluble or only very slightly soluble in water. They dissolve in alcohol, ether, benzene, etc.

The solubility of a compound in water increases with the

increase of oxygen content; especially is this true when the oxygen atoms are combined with hydrogen as in —OH groups.

The homologues of low molecular weight of the aliphatic series, such as alcohols, aldehydes, ketones, amines, and acids, are soluble in water; but the solubilities decrease with increasing molecular weight.

Alkali salts of acids, salts of amines, sugars, polybasic acids, hydroxy acids, sulfonic acids, and polyhydroxy alcohols are soluble in water.

Esters are very slightly soluble in water, but soluble in alcohol and ether.

Ether dissolves very many organic compounds. (Not salts of acids.) It is slightly soluble in water and is used for extracting products from aqueous solutions.

Acid anhydrides are soluble in alcohol and ether.

Fats and oils are insoluble in water, but readily soluble in benzene, ether, chloroform, etc.

Nitro compounds are insoluble in water but soluble in alcohol and ether.

The presence of a sulfonic acid group increases the solubility of an organic compound in water.

The hydroxy derivatives of aromatic hydrocarbons are soluble in water, but more so in alcohol and ether.

The *p*-compounds are less soluble in the various solvents than the isomeric *o*- and *m*- compounds.

Alkaloids are usually insoluble in water, but soluble in alcohol, chloroform, benzene, etc.

Homologues are mutually soluble.

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MULLIKEN—A Method for the Identification of Pure Organic Compounds.  
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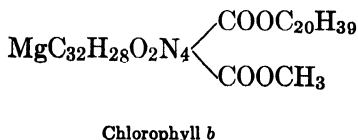
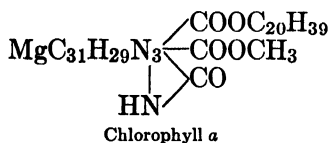
## CHAPTER XXXV

### PLANT AND ANIMAL PIGMENT

CHLOROPHYLL, CAROTIN, XANTHOPHYLL, FLAVONES, ANTHOCYANINS, HEMOGLOBIN AND BILE PIGMENTS

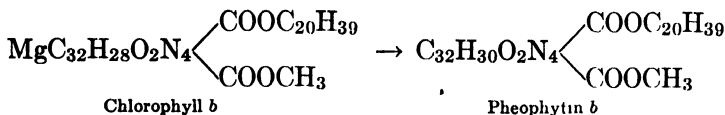
**Chlorophyll.**—The chemistry of chlorophyll, the green pigment in plants, has been worked out by Willstätter and his pupils. Without going into any details, some of the essential points as to its structure and general characteristics may be given.

Chlorophyll is really a mixture of two substances:

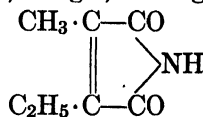


Both contain the element magnesium in organic combination, and both are esters of a tribasic acid, chlorophyllin, combined with phytol,  $\text{C}_{20}\text{H}_{39}\text{OH}$  (an unsaturated alcohol) and methanol.

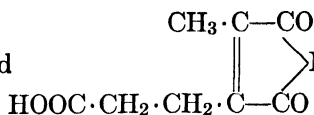
With alkali the ester groups in chlorophyll are hydrolyzed, giving the corresponding carboxylic acids (chlorophyllins). The  $\text{COOH}$  groups can next be removed by heating with alkali. Acids (oxalic or  $\text{HCl}$ ) remove the magnesium from the molecule; e.g.,



When chlorophyll *a* or chlorophyll *b* is oxidized, we get, among other products, methyl ethyl maleinimide



and hematinic acid

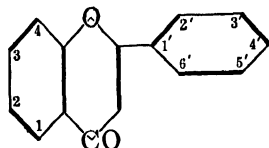


are formed in the oxidation of hemoglobin.

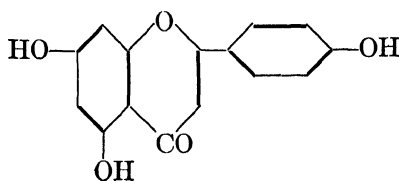
**Carotin** is associated with chlorophyll in the green leaf. It is a hydrocarbon with the formula  $\text{C}_{40}\text{H}_{56}$ .

**Xanthophyll**, also associated with chlorophyll (and carotin), has the formula  $\text{C}_{40}\text{H}_{56}\text{O}_2$ . By oxidation, xanthophyll may be obtained from carotin, and *vice versa* by reduction, xanthophyll yields carotin. It is assumed that both these pigments play an important rôle in plant respiration. (Pigments from the egg yolk and blood serum have been isolated which are identical with carotin and xanthophyll.)

**Flavones.**—A number of yellow substances derived from flavone occur in plants



Some of these are chrysin (1, 3-dihydroxyflavone) which occurs in several varieties of poplar; apigenin (1, 3, 4'-trihydroxyflavone)



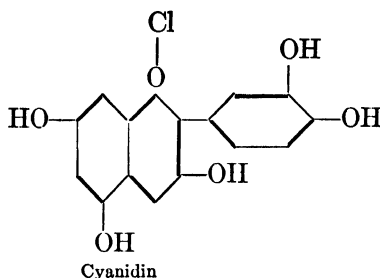
found in parsley and celery in the form of glucosides; etc.

**Anthocyanins** are red, violet and blue pigments present in flowers, fruits, leaves of plants, etc., in the form of glucosides. By hydrolysis, the anthocyanins are converted into glucose (or other monosaccharide) and anthocyanidins.

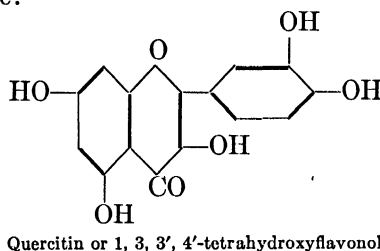
It is believed that these anthocyanins are reduction products of flavones (and *vice versa*, that flavones are oxidation products of anthocyanins), and that changes from one to the other are brought about in the plant by oxidizing and reducing enzymes.



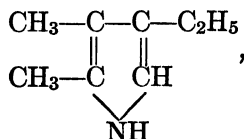
The anthocyanin in the cornflower and the rose is known as "cyanin," and this, on hydrolysis, yields two molecules of glucose and cyanidin (an anthocyanidin):



This cyanidin, Willstätter has also obtained by reducing quercetin, a hydroxyflavone:



**Hemoglobin**, the red pigment in blood, is a combination of hematin, an iron-containing substance, and globin, a protein belonging to the group of histones. It forms compounds with oxygen and carbon monoxide, forming oxyhemoglobin and carboxy-hemoglobin, the latter being the more stable. "Hemin" (or "hematin hydrochloride") is obtained from dried blood by boiling with glacial acetic acid. Very characteristic dark plates and prisms are obtained, which may be identified under the microscope. This method is made use of for the detection of blood. When hemoglobin is treated with  $\text{H}_2\text{SO}_4$ , the iron is set free as ferrous sulfate and hemotoporphyrin, an iron-free hematin, is obtained. From this substance, hemopyrrole,



may be obtained—a substance, which is also a decomposition product obtained from chlorophyll.

**Bile pigments** (bilirubin, biliverdin, bilicyanin, etc.) are the substances which are responsible for the characteristic color of bile. They are formed in the liver and originate from the hemoglobin of the blood. Bilirubin,  $C_{32}H_{36}N_4O_6$ , a reddish-brown pigment, found in abundance in carnivora, is oxidized (even by the oxygen of the air) to biliverdin,  $C_{32}H_{36}N_4O_8$ , a green pigment, found largely in the bile of herbivora. (Hydrobilirubin, a reduced product of bilirubin, is probably isomeric with stercobilin, the pigment of the feces, and with urobilin, a pigment in urine.) The *Gmelin's* test for bile pigments—the play of colors obtained when conc.  $HNO_3$  is added to bile—is dependent upon the production of various colored oxidation products of the type of bilirubin, biliverdin, etc.

**Melanins.**—This group includes several different varieties of amorphous black or brown pigments which are insoluble in water, alcohol, ether, chloroform, dilute acids, and which occur in skin, hair, etc. They are said to be derived from the amino acids tyrosine (p. 148) and tryptophan (p. 312).

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## CHAPTER XXXVI

### ENZYMES, VITAMINS, HORMONES

#### ENZYMES

THESE are catalytic substances produced as a result of cellular activity. They are responsible for many of the chemical changes which occur in the body.

So far enzymes have not been isolated in the pure condition,\* but they can be classified because they are "specific" in their action; that is to say, ptyalin, the enzyme found in saliva, will act on starch and one or two other carbohydrates, but not on proteins, whereas pepsin, the enzyme found in the gastric juice of the stomach, will act on proteins but not on carbohydrates.

A few of the common enzymes, giving their distribution, the substances acted upon ("substrates") and the end products formed, are given on the following page.

The ending *ase* has been adopted to denote an enzyme; for example, *sucrase* is an enzyme, its name also suggesting that it acts on the sugar sucrose. However, old names, such as pepsin, trypsin and rennin, still remain.

Enzymes are soluble in water, dilute salt solutions, dilute alcohol and glycerol. Like the proteins, they are precipitated by ammonium sulfate and concentrated alcohol. They are very easily adsorbed by various substances and show colloidal properties. They are, as a rule, destroyed at the temperature of boiling water, and their action is inhibited, but not destroyed at 0 °C. The enzymes act best (or show an optimum activity) around 37–45° C.

Enzymes are extremely susceptible to changes in hydrogen ion concentrations, and for each enzyme there is a particular  $p_H$  at which its reactivity is at a maximum ("optimum reaction").

\*Recently Nothrop has isolated pepsin and trypsin in what appear to be in pure forms, and the same may be said of Sumner's urease.

For example, the  $p_H$  of trypsin is 8.0, that of pepsin 1.4, and of ptyalin 6.7. Since the neutral point is  $p_H$  7, this means that trypsin acts best in an alkaline solution, whereas pepsin acts best in a decidedly acid solution, and ptyalin is most reactive in a slightly acid medium.

Name and Class	Distribution	Substrate	End-products
Ptyalin	Saliva	Starch, dextrin, etc.	Maltose
Lactase	Intestinal juice and mucosa	Lactose	Glucose and galactose
Maltase	Blood serum, liver, saliva, pancreatic and intestinal juices and lymph	Maltose	Glucose
Sucrase or invertase	Intestinal juice and mucosa	Sucrose	Glucose and fructose
Zymase	Yeast	Sugars	Alcohol, $CO_2$ , etc.
Urease	Micrococcus ureae, soy bean, etc.	Urea	Carbon dioxide and ammonia
Steapsin or lipase	Pancreatic juice	Fats	Fatty acid and glycerol
Catalase	Plant and animal tissues	Hydrogen peroxide	Oxygen or oxidation products
Peroxidase	Plant and animal tissues	Organic peroxides	Active oxygen or oxidation products
Erepsin	Intestinal mucosa and juice, other tissues	Peptids, also peptones and casein	Simpler peptids and amino acids
Rennin	Gastric juice	Casein	Paracasein
Thrombin	Blood	Fibrinogen	Fibrin
Trypsin	Pancreatic juice	Proteins	Proteoses, peptones, peptids, amino acids
Pepsin	Gastric juice	Proteins	Proteoses, peptones, and peptids

## VITAMINS

It has recently been found that besides proteins, fats, carbohydrates and mineral salts, there are other, as yet, ill-defined substances which, though needed in but minute quantities, are essential to life. These substances are known as *vitamins*. At least five vitamins have been detected. For purposes of identification, the vitamins are often called A, B, C, D and E. The presence of all five of these vitamins is essential to well-being. As a matter of fact, very few foods contain all five. Milk is one of the rare exceptions, but even then the quantity of vitamin C which it contains is dangerously small. It is only by eating a variety of foods that we assure ourselves a liberal allowance of all five types of vitamins.

*Vitamin A*.—This is present in abundance in milk, butter, egg-yolk, cod-liver oil, and to a lesser extent, in beef fat and in many vegetable foods (lettuce, spinach, cabbage, carrots, potatoes, etc.). Lard and vegetable oils, such as olive oil are practically devoid of it. Cereals in general (wheat, rye, barley, etc.) contain little. In a general way, the statement may be made that this vitamin is present in green leaves and in the embryos of many seeds. Recently carotin,  $C_{40}H_{56}$ , has been shown to be transformed into vitamin A in the liver.

*Vitamin B*.—This is more abundant than either of the other two. In fact, nearly all natural foods contain some of it. Yeast is particularly rich in this vitamin; so are milk and orange juice. The cereals contain it but only the outer layers, so that in patent flour there is much less of this vitamin than in whole wheat flour. Vitamin B really consists of two vitamins—vitamin  $B_1$ (F), the anti-neuritic vitamin; and vitamin  $B_2$ (G) the anti-pellagra vitamin.

*Vitamin C*.—Most fresh fruits and fresh vegetables contain this vitamin. The emphasis is advisedly put on fresh material. The orange and the tomato are particularly good examples.

*Vitamin D* is present in greatest abundance in cod-liver oil and in much smaller quantity in milk. It is apparently produced when some foods are irradiated with ultra-violet light. Vitamin D is apparently synthesized when ergosterol is irradiated.

*Vitamin E* is particularly present in the wheat germ.

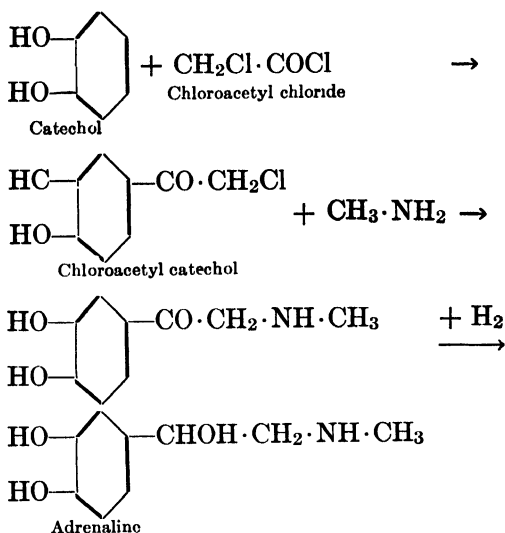
*Effect of heat and oxidation.*—All five vitamins are more or less susceptible to heat, so that any process involving this operation—cooking or canning—is apt to destroy, or greatly lessen, the efficacy of the vitamins. The general experience has been that heating for a long time at a comparatively low temperature is even more harmful than heating for a short time at a comparatively high temperature. Of the five, the vitamin C seems the most susceptible to heat. The activity of a number of the vitamins is lessened by exposure to air or oxidation. This is particularly true of vitamins A and C.

*Diseases due to lack of vitamins.*—Four diseases have been identified as being due to vitamin deficiency. One of them is beri-beri, involving a general paralysis of the system and is due to a lack of vitamin B<sub>1</sub>(F); a second is the vitamin the absence of which gives rise to pellagra—B<sub>2</sub>(G); another is scurvy, involving choppy gums and loose teeth and is due to lack of vitamin C; the fourth is xerophthalmia, and eye disease, involving a lack of vitamin A; and the fifth is rickets, a disease involving faulty bone construction, due to lack of vitamin D. Vitamin E is concerned with the process of reproduction.

## HORMONES

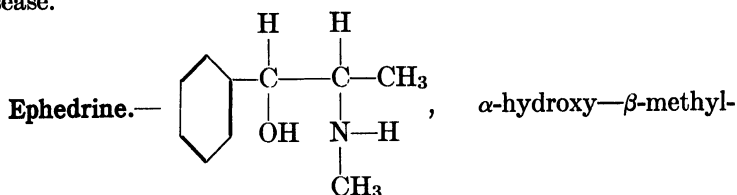
In the body there are various ductless glands (glands without tubes), such as the thyroid, the pituitary, the adrenals, etc., which manufacture specific substances that find their way into the blood stream and influence other organs of the body. The substances so manufactured are called "hormones" (from the Greek "to excite") or "chemical messengers." These hormones profoundly influence various activities of the body. In at least two instances hormones have been isolated in the pure condition.

**Adrenaline.**—One of the hormones of the adrenal glands may be isolated from the latter by first treating concentrated adrenal extracts with alcohol, lead acetate, etc.; then precipitating the active substance by the addition of concentrated ammonia. The precipitate is purified by repeatedly dissolving in acid and reprecipitating with ammonia. The adrenaline may be synthesized by the following reactions:



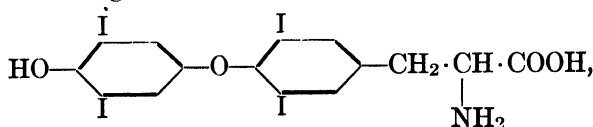
Adrenaline is most frequently used to constrict the blood vessels and thereby increase the blood pressure. It is by far the most powerful known hemostatic (checks bleeding).

Recently an extract from the cortex of the adrenal gland has been obtained which cures a rare ailment known as "Addison's disease."



aminopropylbenzene, or its hydrochloride, has uses similar to adrenaline.

**Thyroxine** is the hormone in the thyroid gland. Kendall has isolated it from the gland. Harington has determined its formula to be



$\beta$ -[3, 5-diiodo-4-(3', 5'-diiodo-4'-hydroxyphenoxy) phenyl- $\alpha$ -aminopropionic acid, and he has also succeeded in synthesizing the substance.

It is administered in diseases involving a deficient secretion of the thyroid gland.

**Insulin.**—This is the hormone present in the pancreas, and its absence, as Banting and Macleod have shown, gives rise to diabetes. Abel has recently obtained insulin in crystalline form, and while he has not yet determined its formula, he and Funk find that it contains a high percentage of sulfur. An extract containing insulin is now universally used in the treatment of diabetes. The extract has to be injected.

**Pituitrin**, an impure extract of the pituitary body, which contains the hormone, is used to promote uterine contractions and to stimulate peristalsis.

The anterior part of the pituitary has recently been shown to consist of at least two hormones, one dealing with the growth process and the other having an accelerating effect on the sex process.

**Secretin** represents a hormone present in the intestinal mucosa which plays an important part in controlling the flow of pancreatic juice into the small intestine, and thereby aids in digestion.

A **parathyroid hormone** has recently been obtained by Collip which seems to play an important part in regulating the calcium metabolism of the body.

Doisy has obtained an active extract (hormone) from the ovaries; and active extracts have also been obtained from the male glands.

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## CHAPTER XXXVII

### NOMENCLATURE OF ORGANIC COMPOUNDS

THE number of organic compounds is in excess of 225,000, and the naming of such compounds presents no little difficulty. Some of the methods adopted for naming organic compounds have been referred to in the various chapters of the book. In the present chapter, the methods adopted will be briefly summarized. In addition, the naming of various groups, and the principles involved in the naming of a number of somewhat complex compounds, will be given. **It is hoped that such an outline will prove of value to the student of chemistry who is about to begin more advanced work in organic chemistry, or in one of its many applications, and who will have occasion to consult the standard reference books and the current literature.**

It would be well, at the outset, for the student to review the chart at the beginning of the book, which gives type formulas. From this chart, as well as from various chapters in the book, we may deduce the following rules:

<i>A word ending in</i>	<i>Indicates</i>
-ane	paraffin
-ene or -ylene	olefin
-ine	acetylene
-diene	diolefin
-diene	diacetylene
-ene	aromatic hydrocarbon (as a rule)
-ol	hydroxyl group
-diol	two hydroxyl groups
-al	aldehyde
-one	ketone (or quinone)
-ic (sometimes -oic)	acid
-ase	enzyme
-ose	sugars
-ate, -ite	salts, esters

In naming<sup>1</sup> a compound so as to indicate that oxygen is replaced

<sup>1</sup> These suggestions are taken from the publications of the *American Chemical Society*.

by sulfur, the prefix *thio* is used; e.g.,  $\text{HCNS}$ , *thiocyanic acid*;  $\text{CS}(\text{NH}_2)_2$ , *thiourea*.

Hydroxyl derivatives of hydrocarbons end in *-ol*, as *glycerol*, *resorcinol*, *pyrocatechol*.

The names of the groups  $\text{NH}_2$ ,  $\text{NHR}$ ,  $\text{NR}_2$ ,  $\text{NH}$  or  $\text{NR}$  end in *-ido* only when they are substituents in an acid group, otherwise in *-ino*; e.g.,  $\text{CH}_3 \cdot \text{C}=\text{NH}$ , ethyl imidoacetate;  $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ ,

$\text{OC}_2\text{H}_5$   $\text{NH}_2$   
 $\beta$ -aminopropionic acid.

*Hydroxy* is used to designate the hydroxyl group; e.g.,  $\text{CH}_2 \cdot \text{COOH}$ , *hydroxyacetic acid*.



Salts of organic bases with hydrochloric acid are called *hydrochlorides*; e.g.,  $\text{NH}_2 \cdot \text{HCl}$ , *aniline hydrochloride*.



Compounds which are not alcohols, but have received names ending in *-ol* are spelled *-ole*, as *anisole*, *indole*.  $\text{C}_6\text{H}_6$  is called *benzene* (not *benzol*),  $\text{C}_7\text{H}_8$  *toluene*, etc.

The endings *-ine* are used for basic substances, and *-in* for glycerides, glucosides, bitter principles, proteins, etc.; e.g., *aniline*, *purine*, *morphine*; but *gelatin*, *palmitin*, *amygdalin*, *albumin*, *protein*.

In naming organic compounds the connective *o* is used in such names of substituent radicals as *amino-*, *bromo-*, *cyano-*, and *iodo-*; e.g., *bromobenzene*, *chloroacetic acid*, *nitroaniline*.

Acid radicals, such as  $\text{C}_6\text{H}_5\text{CO}$ , end in *-yl*, and their compounds with halogens, as  $\text{C}_6\text{H}_5\text{COCl}$ , are called *chlorides*, *bromides*, etc.; e.g., *benzoyl chloride*.

The names *butane*, *pentane*, etc., are used only for the normal hydrocarbons, with the prefix *cyclo-*, for saturated cyclic hydrocarbons.

To designate *ortho-*, *meta-*, *para-*, *dextro-*, *levo-*, *racemic*, *symmetrical*, *secondary*, *tertiary* and *meso*, we use *o-*, *m-*, *p-*, *d-*, *l-*, *dl-*, *sym-*, *sec-*, *tert-* and *meso-*, respectively.

*me*, *et*, etc., are abbreviations for *methyl*, *ethyl*, etc., groups.

Numerals precede the part of the name to which they refer; e.g., *2-bromo-3-methylbenzenesulfonic acid*.

For complex cyclic compounds requiring fixed numberings, the student is referred to Richter's *Lexikon der Kohlenstoff-Verbindungen*, Vol. 1.

The following list gives the names of a number of important organic radicals:<sup>1</sup>

acenaphthenyl  $C_{12}H_9-$

acetamido  $CH_3CONH-$

acetenyl = ethinyl

acetimido  $CH_3C(:NH)-$

acetonyl  $CH_3COCH_2-$

acetoxy  $CH_3CO \cdot O-$

acetyl  $CH_3CO-$

acetylene =  $CH \cdot CH=$

acridyl  $C_{13}H_9N-$

acrylyl  $CH_2 : CHCO-$

adipyl  $-OC \cdot (CH_2)_4 \cdot CO-$

alanyl  $CH_3 \cdot CHNH_2 \cdot CO-$

alkoxy  $RO-$  (*any alkyl radical attached by oxygen*)

allyl  $CH_2 : CH \cdot CH_2-$

$\beta$ -allyl = isopropenyl

amidoxalyl  $H_2N \cdot CO \cdot CO-$

amino (amido)  $H_2N-$

amoxy  $CH_3 \cdot (CH_2)_4 \cdot O-$

amyl  $CH_3 \cdot (CH_2)_4-$  or  $C_5H_{11}$

*tert*-amyl  $\begin{array}{c} CH_3CH_2 \\ \diagup \\ (CH_3)_2C= \end{array}$

amylidene  $CH_3 \cdot (CH_2)_3 \cdot CH=$

anilino  $C_6H_5NH-$

anisal  $p-CH_3O \cdot C_6H_4 \cdot CH=$

anisoyl  $p-CH_3O \cdot C_6H_4 \cdot CO-$

anisyl (*o*, *m* or *p*)  $CH_3O \cdot C_6H_4-$

anisyldiene = anisal

anthranilo  $o-C_6H_4 \begin{array}{c} \diagup CO \\ | \\ N- \end{array}$

anthranoyl  $o-H_2N \cdot C_6H_4 \cdot CO-$

anthraquinonyl (*from anthraquinone*, 2 isomers)

anthryl (*from anthracene*, 5 isomers)

<sup>1</sup> The list is taken from one prepared by the editors of *Chemical Abstracts* or the "Decennial Index" and brought up to date in subsequent editions.



boryl O : B—

bromo Br—

 $\Delta^1$ -butenyl  $\text{CH}_3\text{CH}_2\text{CH} : \text{CH}$ — $\Delta^2$ -butenyl  $\text{CH}_3 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2$ — $\Delta^3$ -butenyl  $\text{CH}_2 : \text{CH} \cdot (\text{CH}_2)_2$ —butoxy  $\text{CH}_3 \cdot (\text{CH}_2)_3 \cdot \text{O}$ —butyl  $\text{CH}_3(\text{CH}_2)_3$ —

$\text{CH}_3\text{CH}_2$   
*sec*-butyl  $\text{CH}_3 \rangle \text{CH}$ —

*tert*-butyl  $(\text{CH}_3)_3\text{C}$ —butylene  $-\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2-$  [1,4-form]butylidene  $\text{CH}_3 \cdot (\text{CH}_2)_2 \cdot \text{CH} =$ butyryl  $\text{CH}_3 \cdot (\text{CH}_2)_2 \cdot \text{CO}$ —camphanyl (*from camphane*)  $\text{C}_{10}\text{H}_{17}$ camphoroyl (*from camphoric acid*)  $\text{C}_8\text{H}_{14}(\text{CO})_2$ :camphoryl (*from camphor*)  $\text{C}_{10}\text{H}_{15}\text{O}$ —camphorylidene (*from camphor*)  $\text{C}_{10}\text{H}_{14}\text{O}$ :carbamido  $\text{H}_2\text{N} \cdot \text{CO} \cdot \text{NH}$ —carbamyl  $\text{H}_2\text{N} \cdot \text{CO}$ —

carbanilino = phenylcarbamyl

carbazyl (*from carbazole, 5 isomers*)  $\text{C}_{12}\text{H}_8\text{N}$ —carbethoxy  $\text{C}_2\text{H}_5\text{O} \cdot \text{OC}$ —carbomethoxy  $\text{CH}_3\text{O} \cdot \text{OC}$ —carbonyl  $\text{OC} =$ carbonyldioxy  $-\text{O} \cdot \text{CO} \cdot \text{O}-$ carboxy  $\text{HO} \cdot \text{OC}$ —

(4)  $(\text{CH}_3)_2\text{CH}$   
*carvacryl*  $\text{CH}_3 \rangle \text{C}_6\text{H}_3-$  (2)

cetyl  $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2$ —

chloro Cl—

chloromercuri  $\text{ClHg}$ —cinnamal  $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{CH} =$ 

cinnamenyl = styryl

cinnamyl  $\text{C}_6\text{H}_5\text{CH} : \text{CHCO}$ —

cinnamylidene = cinnamal

cresotyl (*from cresotic acid*) 2, 3-(OH)(CH<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>CO—

cresoxy = toloxy

cresyl (10 isomers) (*o, m or p*) (HO)(CH<sub>3</sub>)·C<sub>6</sub>H<sub>3</sub>—

cresylene = tolylene

crotonyl  $\text{CH}_3\text{CH} : \text{CHCO}$ —

cumal  $p\text{-(CH}_3)_2\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{CH=}$

cumenyl  $(\text{CH}_3)_2\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{—}$

cuminal = cumal

cyano  $\text{NC—}$

cyclobutyl  $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH—}$

cyclohexenyl (*from cyclohexene, 3 isomers*)  $\text{C}_6\text{H}_9\text{—}$

cyclohexyl (*from cyclohexane*)  $\text{C}_6\text{H}_{11}\text{—}$

cyclohexylidene  $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C=}$

cyclopentenyl (*from cyclopentene*)  $\text{C}_5\text{H}_7\text{—}$

cyclopentyl (*from cyclopentane*)  $\text{C}_5\text{H}_9\text{—}$

cyclopropyl  $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH—}$

cymyl  $\begin{array}{c} (4) (\text{CH}_3)_2\text{CH} \\ (1) \text{CH}_3 \end{array} \text{C}_6\text{H}_3\text{—} (3)$

desyl  $\begin{array}{c} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5\cdot\text{CO} \end{array} \text{CH—}$

diazo  $\text{—N : N—}$

diazoamino = azimino

diazoöxy  $\text{—N}(\text{: O})\text{: N—}$

epoxy  $\text{—O—}$  (*to different atoms already united in some other way*)

ethene = ethylene

ethenyl  $\text{CH}_3\text{C}\equiv$

ethinyl  $\text{CH : C—}$

ethoxalyl  $\text{C}_2\text{H}_5\text{O}\cdot\text{OC}\cdot\text{CO—}$

ethoxy  $\text{C}_2\text{H}_5\text{O—}$

ethyl  $\text{CH}_3\text{CH}_2\text{—}$

ethylene  $\text{—CH}_2\cdot\text{CH}_2\text{—}$

ethylenedioxy  $\text{—O}\cdot(\text{CH}_2)_2\cdot\text{O—}$

ethylidene  $\text{CH}_3\text{CH=}$

fenchyl (*from fenchyl alcohol*)  $\text{C}_{10}\text{H}_{17}\text{—}$

fluoro  $\text{F—}$

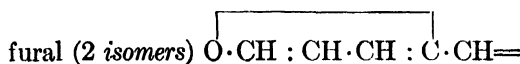
fluorylidene (*from fluorene*)  $\text{C}_{13}\text{H}_8\text{:}$

fluoryl (*from fluorene, 5 isomers*)  $\text{C}_{13}\text{H}_9\text{—}$

formamido  $\text{HCONH—}$

formazyl  $\begin{array}{c} \text{C}_6\text{H}_5\cdot\text{N : N} \\ \text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{N} \end{array} \text{C=}$

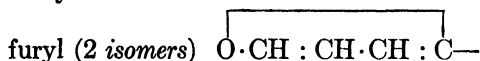
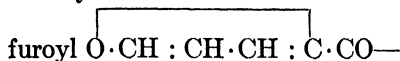
formyl  $\text{OCH—}$



furfural = fural

furfuryl = furyl

furfurylidene = fural



furylidene = fural

geranyl (from geraniol)  $\text{C}_{10}\text{H}_{17} -$

glutamyl  $-\text{OC} \cdot \text{CHNH}_2 \cdot (\text{CH}_2)_2 \cdot \text{CO} -$

glutaryl  $-\text{OC} \cdot (\text{CH}_2)_3 \cdot \text{CO} -$

glyceryl  $-\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 -$

glycolyl  $\text{HOCH}_2 \cdot \text{CO} -$

glycyl  $\text{H}_2\text{NCH}_2 \cdot \text{CO} -$

glyoxyl  $\text{OCH} \cdot \text{CO} -$

guaiacyl = *o*-anisyl

guanido  $\text{H}_2\text{N} \cdot \text{C}(:\text{NH}) \cdot \text{NH} -$

guanyl  $\text{H}_2\text{N} \cdot \text{C}(:\text{NH}) -$

hendecyl  $\text{CH}_3 \cdot (\text{CH}_2)_{10} -$

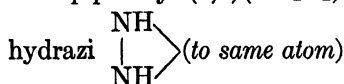
heptyl  $\text{CH}_3 \cdot (\text{CH}_2)_6 -$

hexadecyl = cetyl

hexyl  $\text{CH}_3 \cdot (\text{CH}_2)_5 -$

hippuryl  $\text{PhCONHCH}_2\text{CO} -$

homopiperonyl  $(3,4)(\text{CH}_2\text{O}_2) \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 -$



hydrazino  $\text{H}_2\text{N} \cdot \text{NH} -$

hydrazo  $-\text{HN} \cdot \text{NH} -$  (to different atoms)

hydrazono  $\text{H}_2\text{N} \cdot \text{N} =$

hydroxamino  $\text{HONH} -$

hydroximino = isonitroso

hydroxy (hydroxyl)  $\text{HO} -$

-idene added to any radical usually means a double bond at point of attachment

imidazolyl (from imidazole, 4 isomers)  $\text{C}_3\text{H}_3\text{N}_2 -$

imino (imido)  $\text{NH} =$

indenyl (from indene, 7 isomers)  $\text{C}_9\text{H}_8 -$

indyl (*from indole*, 7 isomers)  $C_8H_6N-$

indylidene (*from indole*)  $C_8H_7N :$

iodo I—

iodoso OI—

iodoxy  $O_2I-$

isoallyl = propenyl

isoamoxy  $(CH_3)_2 \cdot CH \cdot CH_2 \cdot CH_2O-$

isoamyl  $(CH_3)_2 \cdot CH \cdot CH_2 \cdot CH_2-$

isoamylidene  $(CH_3)_2 \cdot CH \cdot CH_2 \cdot CH=$

isobutenyl  $(CH_3)_2 \cdot C=CH-$

isobutoxy  $(CH_3)_2 \cdot CH \cdot CH_2O-$

isobutyl  $(CH_3)_2CH \cdot CH_2-$

isobutyryl  $(CH_3)_2 \cdot CH \cdot CO-$

isocyano C : N—

isodiazon  $\begin{array}{c} N \\ | \\ HN \end{array} \rangle (to\ some\ atom)$

isohexyl  $(CH_3)_2 \cdot CH \cdot (CH_2)_3-$

isoindyl (*from isoindole*, 4 isomers)  $C_8H_6N-$

isoleucyl  $CH_3 \cdot CH_2 \cdot CH(CH_3) \cdot CHNH_2 \cdot CO-$

isonitro  $HOON=$

isonitroso  $HON=$

$\Delta_2$ -isopentenyl  $(CH_3)_2 \cdot CH \cdot CH : CH-$

isophthalal (*m*) =  $HC \cdot C_6H_4 \cdot CH=$

isophthalylidene = isophthalal

isopropenyl  $\begin{array}{c} CH_3 \\ \diagdown \\ C \\ \diagup \\ CH_2 \end{array}$

isopropoxy  $(CH_3)_2 \cdot CHO-$

isopropyl  $(CH_3)_2 \cdot CH-$

isopropylidene  $(CH_3)_2 \cdot C=$

isoquinolyl (*from isoquinoline*, 9 isomers)  $C_9H_6N-$

isothiocyano S : C : N—

isovaleryl  $(CH_3)_2 \cdot CH \cdot CH_2 \cdot CO-$

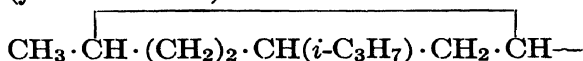
isoxazolyl (*from isoxazole*, 5 isomers)  $C_3H_2ON-$

keto  $O=$  (*to same atom*)

leucyl  $(CH_3)_2 \cdot CH \cdot CH_2 \cdot CHNH_2 \cdot CO-$

malonyl  $-OC \cdot CH_2 \cdot CO-$

menthyl (*from menthane*)





- mercapto HS—  
 mercuri HHg— or —Hg—  
 mesityl (*from mesitylene*) 3,5-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>—  
 methene = methylene  
 methenyl CH≡  
 methionyl —SO<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>—  
 methoxy CH<sub>3</sub>O—  
 methyl CH<sub>3</sub>—  
 methylene CH<sub>2</sub>=  
 methylenedioxy —O·CH<sub>2</sub>·O—  
 methylol = (hydroxymethyl)  
 naphthal C<sub>10</sub>H<sub>7</sub>CH=—  
 naphthalimido (*from naphthalic acid*) C<sub>10</sub>H<sub>6</sub>(CO)<sub>2</sub>N—  
 naphthenyl C<sub>10</sub>H<sub>7</sub>C≡  
 naphthobenzyl C<sub>10</sub>H<sub>7</sub>CH<sub>2</sub>—  
 naphthoxy C<sub>10</sub>H<sub>7</sub>O—  
 naphthoyl C<sub>10</sub>H<sub>7</sub>CO—  
 naphthyl (1- or 2-) C<sub>10</sub>H<sub>7</sub>—  
 naphthylene C<sub>10</sub>H<sub>6</sub>=  
 naphthylidene C<sub>10</sub>H<sub>7</sub>  
 nitramino O<sub>2</sub>N·NH—  
 nitrilo N≡  
 nitro O<sub>2</sub>N—  
*aci*-nitro = isonitro  
 nitroso ON—  
 octyl CH<sub>3</sub>·(CH<sub>2</sub>)<sub>7</sub>—  
 oxalyl —OC·CO—  
 oxamido H<sub>2</sub>N·CO·CONH—  
 oximido = isonitroso  
 oxy —O— (used as a connective; cf. epoxy and keto)  
 pentamethylene —CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>—  
 pentazido  $\text{N}=\text{N}-\text{N}=\text{N}-\text{N}-$   
 pentenyl (*like butenyl*)  
 pentyl = amyl  
 perimidyl (*from perimidine, 8 isomers*) C<sub>11</sub>H<sub>7</sub>N<sub>2</sub>—  
 perthio (*replacing O only*) S : S—  
 phenacyl C<sub>6</sub>H<sub>5</sub>·CO·CH<sub>2</sub>—  
 phenacylidene PhCOCH :  
 phenanthryl (*from phenanthrene, 9 isomers*) C<sub>14</sub>H<sub>9</sub>—

phenanthrylene (*from phenanthrene*)  $C_{14}H_8$  :

phenethyl  $C_6H_5 \cdot CH_2CH_2-$

phenetido  $C_2H_5O \cdot C_6H_4 \cdot NH-$

phenetyl (*o, m* or *p*)  $C_2H_5O \cdot C_6H_4-$

phenoxy  $C_6H_5O-$

phenyl  $C_6H_5-$

phenylazo  $C_6H_5 \cdot N : N-$

phenylcarbamido  $C_6H_5 \cdot NHCONH-$

phenylene (*o*, or *p*)  $C_6H_4=$

phenylenedisazo  $-N : NC_6H_4N : N-$

phenylidene (*o* or *p*)  $\overbrace{CH : CH \cdot CH_2 \cdot CH : CH \cdot C=}$

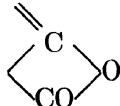
phenylureido = phenylcarbamido

phosphazo  $-N : P-$

phthalal  $=CH \cdot C_6H_4 \cdot CH=$  (*o*)

phthalamido (*o*)  $HO_2C \cdot C_6H_4 \cdot CONH-$

phthalidene (*from phthalide*)  $C_6H_4$



phthalidyl (*from phthalide*)  $\overbrace{C_6H_4CO \cdot O \cdot CH-}$

phthalimido (*o*)  $C_6H_4(CO)_2N-$

phthalyl  $-OC \cdot C_6H_4 \cdot CO-$  (*o*)

picryl (2,4,6)  $(NO_2)_3 \cdot C_6H_2-$

piperidyl (*from piperidine*, 4 isomers)  $C_5H_{10}N-$

piperonyl (3,4)  $(CH_2O_2)C_6H_3 \cdot CH_2-$

piperonylidene (3, 4)  $(CH_2O_2)C_6H_3 \cdot CH=$

pivalyl (*from pivalic acid*)  $(CH_3)_3CCO-$

prolyl (*from proline*)  $\overbrace{NH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH \cdot CO-}$

propargyl  $HC : C \cdot CH_2-$

propenyl  $CH_3 \cdot CH : CH-$

propenylidene  $CH_3CH : C :$

propiolyl  $HC : C \cdot CO-$

propionyl  $CH_3 \cdot CH_2 \cdot CO-$

propoxy  $CH_3 \cdot CH_2 \cdot CH_2O-$

propyl (*n*)  $CH_3 \cdot CH_2 \cdot CH_2-$

propylene  $-CH(CH_3) \cdot CH_2-$

propylidene  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH} =$   
 pseudoallyl = isopropenyl  
*s*-pseudocumyl (1,3,4)  $(\text{CH}_3)_3 \cdot \text{C}_6\text{H}_2 -$   
 pseudoindyl (*from pseudoindole*, 7 isomers)  $\text{C}_8\text{H}_6\text{N} -$   
 pyranyl  $\text{C}_5\text{H}_5\text{O} -$   
 pyrazolyl (*from pyrazole*, 4 isomers)  $\text{C}_3\text{H}_3\text{N}_2 -$   
 pyridyl (*from pyridine*, 3 isomers)  $\text{C}_5\text{H}_4\text{N} -$   
 pyridylidene  $\text{C}_5\text{H}_5\text{N} :$   
 pyrimidyl (*from pyrimidine*)  $\text{C}_4\text{H}_3\text{N}_2 -$   
 pyrroyl  $\text{CH} : \text{CH} \cdot \text{CH} : \text{CH} \cdot \text{N} \cdot \text{CO} -$   
 pyrrol (*from pyrrole*, 3 isomers)  $\text{C}_4\text{H}_4\text{N} -$   
 quinolyl (*from quinoline*, 7 isomers)  $\text{C}_9\text{H}_6\text{N} -$   
 quinonyl = quinoyl  
 quinoxalyl (*from quinoxaline*)  $\text{C}_8\text{H}_5\text{N}_2 -$   
 salicyl (*o*)  $\text{HO} \cdot \text{C}_6\text{H}_4 -$   
 salicylal (*o*)  $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} =$   
 salicylyl (*o*)  $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} -$   
 selenino  $(\text{HO})\text{O} \cdot \text{Se} -$   
 seleno  $\text{Se} =$   
 selenocyano  $\text{NCSe} -$   
 selenono  $(\text{OH})_2\text{OSe} -$   
 selenonyl  $-\text{SeO}_2 -$   
 selenyl  $\text{HSe} -$   
 silicono  $(\text{OH})\text{O} \cdot \text{Si} -$   
 silicyl  $\text{H}_3\text{Si} -$   
 silicylene  $\text{H}_2\text{Si} =$   
 stannyl  $\text{H}_3\text{Sn} -$   
 stearyl  $\text{CH}_3 \cdot (\text{CH}_2)_{16} \cdot \text{CO} -$   
 styrene  $-\text{CH}(\text{C}_6\text{H}_5) \cdot \text{CH}_2 -$   
 styrolene = styrene  
 styryl  $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} -$   
 succinamyl  $\text{H}_2\text{N} \cdot \text{CO} \cdot \text{CH}_2\text{CH}_2 \cdot \text{CO} -$   
 succinyl  $-\text{OC} \cdot \text{CH}_2\text{CH}_2 \cdot \text{CO} -$   
 sulfamino  $\text{HO}_3\text{S} \cdot \text{NH} -$   
 sulfamyl  $\text{H}_2\text{NO} \cdot \text{OS} -$   
 sulfhydryl = mercapto  
 sulfino  $\text{HO}_2\text{S} -$   
 sulfinyl  $\text{OS} =$   
 sulfo  $\text{HO}_3\text{S} -$

sulfonamido  $R \cdot SO_2 \cdot NH-$

sulfonyl  $R \cdot SO_2-$

sulfuryl = sulfonyl

tauryl  $H_2N \cdot CH_2CH_2SO_2-$

telluro  $Te=$

terephthalal (*from terephthalaldehyde*) :  $HCC_6H_4CH :$

tetramethylene = 1,4-butylene

tetrazyl (*from tetrazine, 2 isomers*)  $CHN_4-$

thiazyl (*from thiazole, 3 isomers*)  $C_8H_2NS-$

thienyl (*from thiophene, 2 isomers*)  $C_4H_3S-$

thio  $-S-$

thiocarbonyl  $SC=$

thiocyano  $NCS-$

thiohydroxy = mercapto

thiol (*S replacing O in OH*) } Used in place of "thio" only  
thiono (*S replacing O in CO*) } when required for distinction

thionyl = sulfinyl

thujyl (*from sabinane, attached at 2 position*)  $C_{10}H_{17}-$

thymyl (*from thymol*)  $HO \cdot C : C(CH_3) \cdot CH : CH \cdot C(i-C_3H_7) : C-$

toloxy (*o, m or p*)  $CH_3 \cdot C_6H_4O-$

toluino (*o, m or p*)  $CH_3 \cdot C_6H_4 \cdot NII-$

toluyl (*o, m or p*)  $CH_3 \cdot C_6H_4 \cdot CO-$

$\alpha$ -toluyl  $C_6H_5 \cdot CH_2 \cdot CO-$

tolyl (*o, m and p*)  $CH_3 \cdot C_6H_4-$

$\alpha$ -tolyl = benzyl

tolyene (6 isomers)  $CII_3 \cdot C_6H_3=$

$\alpha$ -tolyene = benzal

triazeno  $NH_2 \cdot N : N-$

triazole  $N : N \cdot N-$

triazolyl (*from triazole*)  $C_2H_2N_3-$

trimethylene  $-CH_2CH_2CH_2-$

tryptophyl (*from tryptophan*)  $C_{11}H_{11}O_2N_2-$

tyrosyl (*from tyrosine*)  $p-HO \cdot C_6H_4 \cdot CH_2CHNH_2 \cdot CO-$

undecyl = hendecyl (in sense  $C_{11}H_{23}-$ )

uramino = carbamido

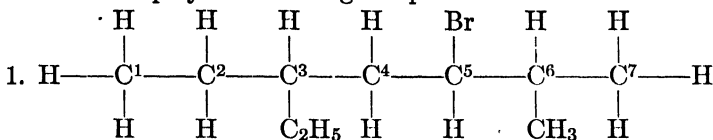
ureido (*by some used synonymously with carbamido*)

$-NH \cdot CO \cdot NH-$

valeryl  $CH_3 \cdot (CH_2)_3 \cdot CO-$

valyl (from *valine*)  $(\text{CH}_3)_2 \cdot \text{CH} \cdot \text{CHNH}_2 \cdot \text{CO}-$   
 vanillal (3,4)  $(\text{CH}_3\text{O})(\text{HO}) \cdot \text{C}_6\text{H}_3 \cdot \text{CH}=\text{}$   
 vanilloyl (3,4)  $(\text{CH}_3\text{O})(\text{HO}) \cdot \text{C}_6\text{H}_3 \cdot \text{CO}-$   
 vanillyl (3,4)  $(\text{CH}_3\text{O})(\text{HO}) \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2-$   
 veratral (3,4)  $(\text{CH}_3\text{O})_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}=\text{}$   
 veratroyl (3,4)  $(\text{CH}_3\text{O})_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CO}-$   
 veratryl (3,4)  $(\text{CH}_3\text{O})_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2-$   
 veratrylidene = veratral  
 vinyl  $\text{H}_2\text{C} : \text{CH}-$   
 vinylene  $-\text{CH} : \text{CH}-$   
 vinylidene  $\text{H}_2\text{C} : \text{C} :$   
 xanthyl (from *xanthene*, 6 isomers),  $\text{C}_{13}\text{H}_9\text{O}-$   
 xyloyl (from *xylic acid*, 7 isomers)  $(\text{CH}_3)_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CO}-$   
 xylyl (9 isomers)  $(\text{CH}_3)_2 \cdot \text{C}_6\text{H}_3-$   
 xylylene  $-\text{H}_2\text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2-$

We shall now illustrate with a number of examples some of the methods employed in naming compounds:

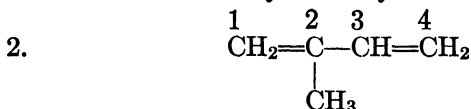


(a) In naming this compound, first select the longest straight chain. In this case, it would be a seven-carbon chain. Therefore, the naming will center around the saturated hydrocarbon heptane.

(b) Consider the elements and groups other than hydrogen as substituents.

(c) Therefore the name of this compound becomes:

3-ethyl-6-methyl-5-bromoheptane

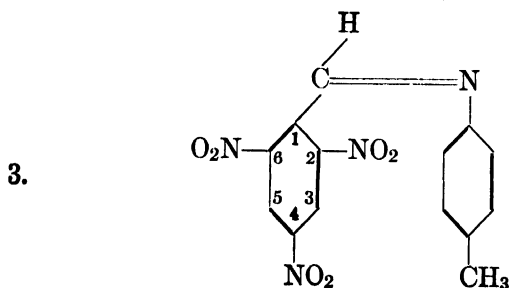



(a) Selecting the longest chain, we have four carbon atoms.

(b) Since there are two double bonds in this chain, the name of the compound must end in *-diene* and center around the unsaturated hydrocarbon butadiene.

(c) The name of this compound becomes 2-methyl butadiene.

(d) But to indicate the positions of the double bonds, the final name becomes 2-methyl-1, 3-butadiene (isoprene).

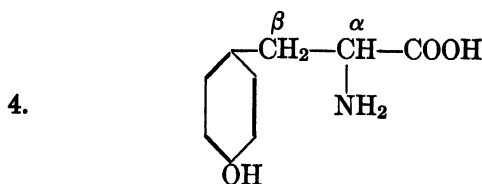


(a) This compound contains the benzal  (divalent)

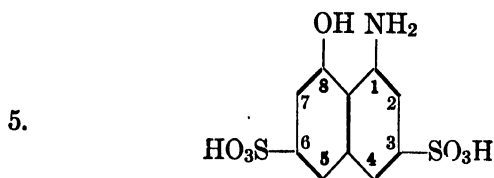
group wherein the three hydrogens in positions 2, 4, 6, are replaced by three nitro groups.

(b) In addition, we have *p*-toluidine, where in place of the two hydrogens in the amino group, there is a double bond.

(c) Therefore, the name of this compound becomes 2, 4, 6-trinitrobenzal-*p*-toluidine.

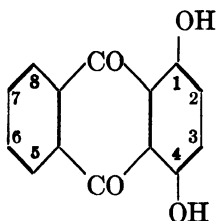


This compound is named  $\alpha$ -amino- $\beta$ -*p*-hydroxyphenylpropionic acid (tyrosine), because it has an amino group attached to the  $\alpha$ -carbon atom and the *p*-hydroxyphenyl group attached to the  $\beta$ -carbon atom.



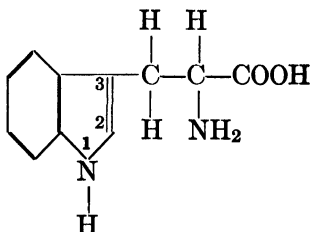
This compound is named 1-amino-8-hydroxy-3,6-naphthalenedisulfonic acid. ("H-acid")

6.



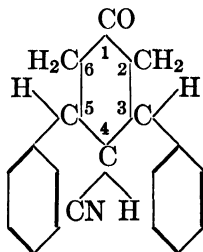
This compound is named 1, 4-dihydroxyanthraquinone (quinizarin.)

7.



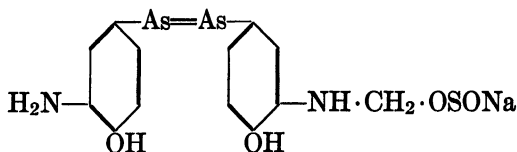
This compound is named  $\alpha$ -amino- $\beta$ -3-indolepropionic acid (Tryptophan).

8.



This compound is named 3,5-diphenyl-4-cyanocyclohexanone-1.

9.



This compound is named sodium 3, 3'-diamino-4, 4'-dihydroxyarsenobenzene-N-methylenesulfinate.

## READING REFERENCE

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# APPENDIX

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## GLOSSARY

**Active principles** include carbohydrates, alkaloids, glucosides organic acids, resins, oils and fats, volatile oils, protein bodies and ferments.

**Analgesics** are drugs which relieve pain when absorbed into the blood.

**Anesthetics** are drugs which produce insensibility to pain. (Local anesthetics are drugs which produce insensibility to pain at the site of application.)

**Anodynes** are drugs which relieve pain when applied locally. They are usually milder in action than the analgesics.

**Antacids** are drugs which neutralize acids.

**Antidote** is an agent which affects a poison either physically or chemically or both so as to remove it from the body or alter its character by forming with it an insoluble or inert compound.

**Antifebrin** is another name for acetanilide (used to decrease fever).

**Antipyretics** are drugs which reduce fever.

**Antiscorbutic** is an agent effective against scurvy.

**Antiseptics** are substances which check the growth of bacteria.

**Antispasmodics** are drugs which lessen contractions of muscles, and also lessen convulsions.

**Aperients** are substances which produce mild movements of the bowels.

**Aromatics** are spicy substances which increase the secretion of the stomach and the intestines.

**Astringents** are drugs which contract or harden the tissues.

**Bactericide** is an agent which destroys bacteria.

**Balsams** are semi-fluid, resinous and fragrant vegetable juices of many varieties.

**Bitters** are drugs which increase the appetite because of their bitter taste.

**Cardiac stimulants** are drugs which increase the activity of the heart.

**Cardiac depressants** are drugs which lessen the heart action.

**Carminatives** are drugs which produce a feeling of comfort in the stomach and relieve the formation of gas in the stomach and the intestines.

**Catabolism** is the breaking down of tissue material in the body.

**Cathartics** are drugs which cause movements of the bowels.

**Caustics** are substances which burn or destroy tissues.

**Counterirritants** are drugs which act on the skin.

**Cyanosis** signifies "blueing" of the skin.

**Deodorants** are remedies which destroy unpleasant odors.

**Disinfectants** are drugs which check the growth of bacteria.

**Diuretics** are drugs which increase the flow of urine.

**Emetics** are drugs which produce vomiting.

**Expectorants** are drugs which increase coughing and bronchial secretions.

**Febrifuges** are drugs which reduce fever.

**Gums** are amorphous, transparent substances which are widely disseminated in plants.

**Hemostatics** are substances which check bleeding.

**Hypnotics** are drugs which produce sleep.

**Lachrymator** is a substance which produces the secretion and discharge of tears.

**Lacteal** is any one of the intestinal lymphatics which absorbs fats.

**Laxatives** are drugs which produce mild movements of the bowels.

**Myotics** are drugs which narrow (contract) the pupil of the eye.

**Mydriatics** are drugs which widen (dilate) the pupil of the eye.

**Narcosis** is the state of profound unconsciousness produced by a drug.

**Narcotic** is a drug which produces stupor or complete insensibility.

**Parasiticide** is an agent which destroys the animal and vegetable parasites found upon the human body.

**Peristalsis** is the worm-like movement by which the alimentary canal propels its contents.

**Purgatives** are drugs which produce moderately active and frequent movements of the bowels.

**Putrefaction** is the decomposition of animal or vegetable substances effected largely through micro-organisms, and resulting in the production of various solids, liquids and gases, some of which have a foul odor.

**Refrigerants** are substances which relieve thirst and cool the patient, in fever.

**Resins** are complex bodies of resinous character. They are generally considered to be oxidation products of hydrocarbons such as terpenes.

**Respiratory stimulants** are drugs which increase the depth and frequency of breathing.

**Respiratory depressants** are drugs which lessen the frequency and depth of breathing.

**Rubefacients** are drugs which redden the skin by widening (dilating) the capillaries.

**Sedatives** are drugs which lessen the activity of an organ or part of the body.

**Somnifacients** or **Soporifics** are drugs which produce sleep.

**Styptics** are substances which stop bleeding.

**Trypanocidal power** is the power possessed by certain bodies of destroying certain parasites found in the blood of man and of animals.

**Vaso-constrictor** is a drug which increases arterial pressure.

**Vaso-dilator** is a drug which lowers arterial tension.

**Vermicides** are drugs which destroy worms.

**Vertigo** means dizziness.

**Vesicatories** or **Vesicants** are drugs which produce blisters.

## BOILING AND MELTING POINTS OF A NUMBER OF ORGANIC COMPOUNDS

Since very few physical constants are given in the body of the work, we shall here give the boiling and melting points of a number of compounds which the student is apt to encounter.<sup>1</sup>

NAME	m. p., ° C.	b. p., ° C.
Acetaldehyde.....	-120	21
Acetamide.....	82	222
Acetanilide.....	114	305
Acetic acid.....	16.7	119
Acetic anhydride.....		139
Acetone.....	- 94	55.6
Acetonitrile.....	- 45	81
Acetyl chloride.....		55
Allyl alcohol.....	-129	96
Amyl acetate.....	- 75	148
Aniline.....	- 6.5	184.4
Aniline hydrochloride.....	198	245
Anthracene.....	216	360
Anthraquinone.....	285	380
Benzaldehyde.....	- 13.5	179
Benzene.....	5.4	80.4
Benzenesulfonic acid.....	52	
Benidine.....	127	400
Benzoic acid.....	121	249
Butyl alcohol.....	- 79	116
Camphor.....	176	209
Carbon disulfide.....	-111	46
Carbon tetrachloride.....	- 23	78
Chloroform.....	- 63	61
Cinnamic acid.....	133	300
Citric acid.....	153	decomposes
<i>o</i> -Cresol.....	30	191
<i>m</i> -Cresol.....	11	202
<i>p</i> -Cresol.....	35	202
<i>p</i> -Cymene.....	- 73	175
Dimethylaniline.....	2	194
Diphenyl.....	70.5	254
Ethyl acetate.....	- 82	77
Ethyl alcohol.....	-114	78.4
Ethyl bromide.....	-115	45
Ethyl butyrate.....	- 93	120

<sup>1</sup> For others, consult Olsen—Chemical Annual (Van Nostrand).

NAME	m. p., ° C.	b. p., ° C.
Ethyl chloride.....	-140	12.5
Ethyl ether.....	-116	35
Ethyl iodide.....	-118	72
Ethylene glycol.....	- 17	199
Formaldehyde.....	.....	- 21
Formic acid.....	7.5	100
Furfural.....	- 36	55 (17 mm.)
Glucose.....	146	
Glycerol.....	17	291
Hydrocyanic acid.....	- 10	26
Iodoform.....	119	sublimes
Isoamyl alcohol.....	-117	131
Isopropyl alcohol.....	- 85	83
Lactic acid.....	18	119 (12 mm.)
Methanol.....	- 95	65
Methyl iodide.....	- 66	45
Methyl salicylate.....	- 8	222
Naphthalene.....	80	218
$\alpha$ -Naphthol.....	96	279
$\beta$ -Naphthol.....	122	285
$\alpha$ -Naphthylamine.....	50	300
$\beta$ -Naphthylamine.....	111	306
Nitrobenzene.....	5	210.8
Oxalic acid.....	189	150 + sub.
Phenol.....	45	182.6
Phthalic acid.....	213	
Phthalic anhydride.....	131	284.5
Pyridine.....	- 42	116
Pyrogallol.....	132.5	293
Resorcinol.....	118	280
Saccharin.....	228 dec.	sub.
Salicylic acid.....	157	sub.
Sulfanilic acid.....	288	
Thymol.....	50	231.8
Toluene.....	- 93	111
<i>o</i> -Toluidine.....	- 21	199.7
<i>m</i> -Toluidine.....	- 13	203
<i>p</i> -Toluidine.....	45	200
Urea.....	132	dec.
Vanillin.....	81	285 dec.
<i>o</i> -Xylene.....	- 27	144
<i>m</i> -Xylene.....	- 53	139
<i>p</i> -Xylene.....	15	138



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## INDEX

### A

Accelerator, 238  
 Acenaphthene, 303  
 Acetaldehyde, 76, 81  
 Acetamide, 114, 118  
 Acetanilide, 237  
 Acetic acid, chart, facing p. 90  
 Acetic acid, 90  
     glacial, 90  
 Acetic anhydride, 114  
 Acetoacetic acid, 134  
 Acetoacetic ester, 134  
     uses, 135  
 Acetone, chart, facing p. 84  
 Acetone, 76, 84  
 Acetonitrile, 161  
 Acetophenone, 262  
 Acetyl acetic acid, 134  
 Acetyl chloride, 115  
     preparation, 116  
     properties, 116  
 Acetylene, 31, 35, 36  
     series, 35  
 Acetylides, 37  
 Acetyl salicylic acid, 288  
 Acid amides, 117  
     identification, 348  
     preparation, 118  
     properties, 118  
 Acid anhydrides, 113  
     identification, 348  
     preparation, 114  
 Acid imides, identification, 348  
 Acids, 85  
     identification, 347  
     nomenclature, 85  
     preparation, 87  
     properties, 88  
     substituted, 86

Acids,  
     type of, 87  
 Acids, aromatic, 268  
 Acids, dibasic, unsaturated, 94  
 Acids, halogen substituted, 123  
     preparation, 123  
     properties, 124  
 Acids, monobasic, 87  
 Acids, table, 89  
 Acids, unsaturated, monobasic, 91  
 Acridine, 313  
 Acriflavine, 313  
 Acrolein, 65, 83, 109  
 Aerolite, 252  
 Acrylaldehyde, 83, 109  
 Acrylic acid, 83, 91, 127  
 Acyl halides, 115  
     identification, 348  
 Adenine, 156  
 Adrenaline, 360  
 Agar-agar, 184  
 Alanine, 147  
 Albolene, 29  
 Albumins, 149  
 Albuminoids, 150  
 Alcohol, denatured, 62  
     ethyl, 59  
     preparation, 59  
 Alcohols, 49  
     absolute, 61  
     aromatic, 248  
     identification, 345  
     nomenclature, 49  
     polyatomic, 65  
     preparation, 54  
     primary, 51  
     properties, 57  
     secondary, 52  
     table, 58

- Alcohols,
  - tertiary, 52
- Aldehydes, 73
  - aromatic, 259
  - properties, 260
  - identification, 346
  - nomenclature, 73
  - preparation, 75
  - properties, 76
- Aldol, 82
  - condensation, 82, 192
- Aliphatic compounds, 16
- Alizarin, 323, 326
- Alkaloids, 335
  - identification, 351
- Alkyl cyanides, 161
  - preparation, 161
  - properties, 162
- Alkyl halide, 41
  - preparation, 42
  - properties, 43
  - table, 42
- Alkyl isocyanides, 162
  - preparation, 162
  - properties, 162
- Allantoin, 158
- Allonal, 121
- Alloxan, 158
- Allyl alcohol, 83
- Allyl ether, 72
- Allyl isothiocyanate, 164, 197
- Aluminum carbide, 18
- Amidol, 284
- Amines, aliphatic, 138
  - aromatic, 234
  - preparation, 235
  - identification, 349
  - preparation, 138
  - primary, 138
  - properties, 139, 141
  - secondary, 140
  - tertiary, 140
  - types, 138
- Amino acid, table, 152
- Amino acids, 143
  - nomenclature, 143
  - preparation, 143
  - properties, 144
- Aminoanthraquinones, 303
- Aminonaphthalenes, 297
- Aminophenols, 283
- Ammonium carbamate, 191
- Ammonium cyanate, 1
- Amphi-naphthoquinone, 299
- Amygdalin, 176
- Amyl butyrate, 102
- Analysis, elementary, 10
  - proximate, 10
  - ultimate, 10
- Anesthesine, 289
- Anethole, 283
- Anhydrides, inner, 125
- Aniline, 232, 236
- Aniline hydrochloride, 237
- Anisaldehyde, 286
- Anisole, 251, 257
- Anthocyanins, 354
- Anthracene, 301
- Anthracenesulfonic acids, 302
- Anthranilic acid, 290, 311
- Anthraquinone, 302
- Anthraquinonesulfonic acids, 303
- Antifebrin, 237
- Antipyrine, 306
- Apigenin, 354
- Applications of organic chemistry, 4
- Arabinose, 167
- Arabitol, 67
- Arbutin, 176
- Arginine, 149
- Aromatic compounds, 16
- Arsanilic acid, 338
- Arsenic compounds, 197, 338
- Arsenophenylglycine, 338
- Artificial silk, 181
- Aseptol, 282
- Aspartic acid, 148
- Aspirin, 288
- Asymmetric carbon atom, 128
- Atoxyl, 338
- Atropine, 336
- Auramine, 320
- Auxochrome group, 317
- Azobenzene, 232, 246
- Azo compounds, 241
  - identification, 350

Azo compounds,  
  reactions, 246  
Azoxybenzene, 232, 246

## B

Baekeland, portrait, 253  
Baeyer, portrait, 310  
Baeyer-205, 327  
Bakelite, 80, 252  
Barbital, 121  
Bases, organic, 138  
Beckmann rearrangement, 263  
Beeswax, 109  
Benedict's reagent, 173  
Benzal chloride, 227  
Benzaldehyde, 259  
Benzaldoxime, 261  
Benzamide, 270  
Benzanilide, 264  
Benzene, 203, 211, 213  
  constitution, 203  
  preparation, 214  
  structure, 205  
Benzenediazonium chloride, 236  
Benzenedisulfonic acid, 228  
Benzenesulfonic acid, 228  
Benzenesulfonyl chloride, 229  
Benzidine, 246  
Benzine, 211  
Benzohydrol, 249  
Benzoic acid, 268  
Benzoic anhydride, 270  
Benzoin, 264  
Benzol, 211  
Benzonitrile, 270  
Benzophenone, 249, 263, 270  
Benzoquinone, 265, 267  
Benzotrichloride, 227  
Benzoylbenzoic acid, 302  
Benzoyl chloride, 270  
Benzoyl peroxide, 271  
Benzyl alcohol, 248  
Benzylamine, 234  
Benzyl bromide, 228  
Benzyl chloride, 222, 227  
Benzyl cyanide, 272  
Benzylidene chloride, 227  
Benzylphenylamine, 234

Betaine, 111  
Bile pigments, 356  
Biuret, 120  
  reaction, 120, 152  
Bogert, portrait, 202  
Boiling points, 382  
Borneol, 332  
Bromal, 82  
Bromoacetone, 228  
Bromoanthracenes, 302  
Bromoethyl methyl ketone, 228  
Bromoform, 47  
Brucine, 336  
Butanes, 23  
Butanol, 63  
Butanone, 74  
Butenes, 35  
Butines, 38  
Butter yellow, 320  
Butylenes, 35  
Butyn, 290  
Butyraldehyde, 74  
Butyric acid, 91, 104, 190  
Butyrolactam, 147  
Butyrolactone, 128

## C

Cacodyl, 198  
Cacodyl oxide, 198  
Cadaverine, 142  
Caffeine, 159  
Calcium carbide, 38  
Calcium cyanamide, 161  
Calcium cyanide, 161  
Calcium formate, 76  
Camphor, 331  
Candles, 91  
Cane sugar, 178  
Cannizzaro reaction, 261  
Caproic acid, 189  
Caramel, 179  
Carbamic acid, 119  
Carbazole, 301, 313  
Carbinol, 50, 58  
Carbocyclic compounds, 200  
Carbohydrates, 166, 186  
  identification, 349  
Carbon monoxide, 90, 117, 163

- Carbon tetrachloride, 47  
Carbonyl group, 73  
Carboxyl group, 85  
Carboxylic acids, 347  
Carbylamine, 162  
    reaction, 140  
Carnauba wax, 109  
Carnaubyl alcohol, 109  
Carotin, 354  
Carvone, 331  
Catalase, 358  
Celluloid, 184  
Cellulose, 181  
Cellulose acetate, 182  
Cellulose nitrate, 182  
Cellulose products, 183  
Cellulose xanthate, 197  
Cephalin, 111  
Cerasin, 111  
Cetyl alcohol, 63, 109  
Chinese wax, 109  
Chitin, 180  
Chloral, 81  
Chloral alcoholate, 82  
Chloral hydrate, 82  
Chloramine-T, 282  
Chloretone, 46  
Chloroacetic acids, 123  
Chloroacetic anhydride, 126  
Chloroacetone, 228  
Chloroacetophenone, 228, 262  
Chloroacetyl chloride, 126  
Chloroanilines, 278  
Chloroanthracenes, 302  
Chlorobenzene, 226  
Chlorobenzyl chloride, *p*-, 228  
Chloroform, 45  
    preparation, 45  
    properties, 46  
    uses, 46  
Chloromalonyl chloride, 126  
Chloronaphthalenes, 296  
Chlorophyll, 353  
Chloropicrin, 228  
Chloroprene, 40  
Chlorotoluenes, 223, 227, 278  
Cholesterol, 111  
Choline, 110  
Chondroitin, 180  
Chromophore group, 317  
Chromotropic acid, 299  
Chrysaniline, 322  
Chrysene, 303  
Chrysin, 354  
Chrysoidine, 319  
Cinchonine, 336  
Cinnamaldehyde, 261  
Cinnamic acid, 272  
Cinnamyl alcohol, 249  
Cis-form, 94  
Citral, 83, 332  
Citrene, 332  
Citric acid, 126, 133  
Citronellal, 332  
Closed chain compounds, 200  
Coal, destructive distillation, 6, 211  
Coal gas, 18  
Cocaine, 336  
Codeine, 337  
Collodion, 184  
Cologne spirit, 59  
Colophony, 329  
Congo red, 320, 325  
Coniine, 336  
Cordite, 184  
Coumarin, 308  
Cream of tartar, 133  
Creatine, 121  
Creatinine, 121  
Cresols, 252  
Cresylic acid, 254  
Crisco, 107  
Crotonic acid, 91, 125  
Crude oil, 27  
Crystal violet, 321  
Cyanamide, 161  
Cyanides, 160  
    identification, 350  
Cyanidin, 355  
Cyanin, 355  
Cyanogen, 160  
Cyanogen chloride, 161  
Cyanuric acid, 164  
Cyclic compounds, 200  
Cyclobutane, 201  
Cyclohexane, 201



Cycloparaffins, 201  
 Cyclopentane, 201  
 Cymene, 217, 328  
 Cystine, 148  
 Cytosine, 156

## D

De-amination, 190  
 Decalin, 299  
 Denatured alcohol, 62  
 Developer Z, 306  
 Dextrins, 180  
 Dextrose. *See* Glucose.  
 Diacetic acid, 134, 190  
 Diamines, 142, 240  
 Diaminobenzenes, 240  
 Diastase, 59  
 Diazoaminobenzene, 245  
 Diazobenzene chloride, 242  
 Diazo compounds, 241  
 Diazo reactions, 241  
 Diazotization, 242  
 Dibromobenzene, *p*-, 228  
 Dichloramine-T, 282  
 Dichloroacetic acid, 123  
 Dichlorobenzene, *p*-, 226  
 Dichlorodifluoromethane, 47  
 Dichloroethyl sulfide, 196  
 Dichloromethyl ether, 228  
 Diethyl nitrosoamine, 141  
 Diethyl phthalate, 273  
 Diethyl sulfate, 101, 255  
 Dihydrobenzene, 218  
 Dimethylamine, 140  
 Dimethylammonium iodide, 140  
 Dimethylaniline, 234, 239  
 Dimethyl glyoxal, 82  
 Dimethyl glyoxime, 83  
 Dimethyl ketone, 84  
 Dimethyl sulfate, 101, 228  
 Dinitrobenzenes, 231  
 Dionine, 337  
 Dipeptide, 151  
 Diphenyl, 218  
 Diphenylacetylene, 217  
 Diphenylamine, 234, 240  
 Diphenylcarbinol, 249, 263  
 Diphenylchloroarsine, 228, 342

Diphenylethane, 218  
 Diphenylethylene, symmetrical, 217  
 Diphenylguanidine, 238  
 Diphenylmethane, 217  
 Dippel's oil, 305, 307  
 Disaccharides, 166  
 Disodium salicylate, 288  
 Distillation, destructive, 6  
     fractional, 7  
 "Duco," 184  
 Dulcin, 285  
 Dyes, 314  
     acid, 316  
     adjective, 314  
     artificial, 314  
     basic, 316  
     direct cotton, 316  
     ingrain, 317  
     mordant, 317  
     natural, 314  
     substantive, 314  
     sulfur, 317  
     theory, 317  
     uses, 316  
     vat, 317  
 Dyes, acridine, 322  
     anthraquinone, 323  
     azine, 323  
     azo, 319  
     diphenylmethane, 320  
     indigo, 324  
     indophenol, 322  
     nitro, 318  
     nitroso, 318  
     oxazine, 322  
     pyrazolone, 319  
     quinoline, 322  
     stilbene, 319  
     sulfur, 323  
     thiazine, 323  
     triphenylmethane, 321  
     xanthene, 321  
 Dynamite, 66

## E

Ehrlich, 4, 339  
 Elements in organic compounds, 8  
 Emetine, 337

- Enzymes, 357**  
     table, 358  
**Ephedrine, 361**  
**Erepsin, 358**  
**Ergosterol, 112**  
**Erythritol, 67**  
**Essential oils, table of, 333**  
**Esterification, 102**  
**Esters, 99**  
     identification, 348  
     preparations, 100  
     properties, 100  
**Ethane, 20**  
**Ethanol, 59**  
**Ethenol, 67**  
**Ethereal salts, 100**  
**Ethers, 69**  
     aromatic, 257  
     identifications, 346  
     manufacture, 70  
     mixed, 69  
     preparation, 69  
     properties, 71  
     uses, 71  
**Ethyl acetate, 102, 114**  
**Ethyl alcohol, 59**  
     chart, facing p. 60  
     manufacture, 60  
     percentages in beverages, 62  
     properties, 61  
     uses, 61  
**Ethylamine, 138, 162**  
**Ethylbenzene, 216**  
**Ethyl benzenesulfonate, 229**  
**Ethyl benzoate, 269, 271**  
**Ethyl bromide, 44**  
**Ethyl butyrate, 102**  
**Ethyl carbonate, 117**  
**Ethyl chloride, 44**  
**Ethyl chloroacetate, 126**  
**Ethyl dichloroarsine, 198**  
**Ethyl ether, 69**  
**Ethyl formate, 102**  
**Ethyl gas, 199**  
**Ethyl hydrogen sulfate, 100**  
**Ethyl lactate, 129**  
**Ethyl malonate, 103**  
**Ethyl methyl carbinol, 55**  
**Ethyl nitrate, 101**  
**Ethyl nitrite, 100, 162**  
**Ethyl nonyl ketone, 75**  
**Ethyl oxalate, 103**  
**Ethyl oxide, 69**  
**Ethyl propyl ether, 69**  
**Ethyl salicylate, 288**  
**Ethyl sulfide, 194**  
**Ethyl sulfuric acid, 101**  
**Ethylene, chart, facing p. 142**  
**Ethylene, 32**  
     preparation, 32, 33  
     properties, 33, 34  
**Ethylene acetate, 103**  
**Ethylene bromide, 44**  
**Ethylene chlorohydrin, 64**  
**Ethylene cyanide, 94**  
**Ethylene oxide, 64, 304**  
**Ethylenediamine, 142**  
**Ethylene dichloride, 45**  
**Ethylene glycol, 63**  
**Ethylene nitrate, 64**  
**Eugenol, 283**
- F**
- Fats, 105, 188**  
     properties, 108  
     table, 106  
**Fehling test, 82, 172**  
**Fermentation, 7, 59**  
**Ferric ammonium citrate, 134**  
**Fire damp, 18**  
**Fischer, portrait, 145**  
**Fittig, synthesis, 211, 225**  
**Flavones, 354**  
**Foodstuffs, 186**  
**Formaldehyde, 80**  
     chart, facing p. 80  
**Formalin, 80**  
**Formic acid, 89**  
**Formula, empirical, 11**  
     molecular, 11  
     structural, 23  
**Friedel-Crafts' reaction, 212, 262, 263,**  
     269, 301  
**Fructose, 177**  
**Fulminic acid, 164**  
**Fumaric acid, 94**

Furan, 304  
 Furfural, 304  
 Fusel oil, 62

## G

Galactans, 184  
 Galactose, 177  
 Gallic acid, 255, 293  
 Gamma sugars, 175  
 Gasoline, 28  
   purification, 28  
 Geranial, 83  
 Geraniol, 332  
 Germanium tetrapropyl, 199  
 Globulins, 149  
 Glossary, 379  
 Glucides, 166  
 Gluconic acid, 174  
 Glucosamine, 177  
 Glucosazone, 169  
 Glucose, 167  
   proof of structure, 168  
   properties, 169, 172  
 Glucosides, 176  
   identification, 349  
 Glucosone, 170  
 Glutamic acid, 148  
 Glutaric acid, 94  
 Glutelins, 150  
 Glyceraldehyde, 187  
 Glyceric acid, 127  
 Glycerol, 65, 99  
   properties, 65  
   uses, 65  
 Glyceryl phosphate, 101  
 Glyceryl trinitrate, 101  
 Glycine, 147  
 Glycine anhydride, 147  
 Glycocol, 147  
 Glycogen, 181  
 Glycol dinitrate, 66  
 Glycol ether, 72  
 Glycolic acid, 126, 128  
 Glycolide, 127  
 Glycoproteins, 150  
 Glycuronic acid, 174  
 Glycylglycine, 151  
 Glyoxal, 82

Glyoxylic reaction, 153  
 Gomberg, 218  
   portrait, 219  
 Griess', diazo reaction, 241  
 Grignard's, reagent, 44  
   portrait, 46  
   reaction, 55  
 Guaiacol, 282  
 Guanidine, 121  
 Guanine, 157  
 Gum arabic, 184  
 Gum tragacanth, 184  
 Gums, 184  
 Gun-cotton, 182

## H

H acid, 299  
 Halogen compounds, 222  
   identification, 345  
 Halogen substituted acids, 123  
   preparations, 123  
   properties, 124  
 Hemicellulose, 184  
 Hemoglobin, 150, 355  
 Heroine, 337  
 Heterocyclic compounds, 200, 304  
 Hexahydrobenzene, 220  
 Hexamethylene, 220  
 Hexamethylenetetramine, 80  
 Hexaphenylethane, 218  
 Hexylresorcinol, 255  
 Hippuric acid, 271  
 Histidine, 149  
 Histones, 150  
 Hofmann reaction, 118, 139, 290, 311  
 Homatropine, 336  
 Homologous series, 25  
 Hopkins-Cole reaction, 153  
 Hormones, 360  
 Hydrazobenzene, 232, 246  
 Hydrobenzamide, 260  
 Hydrocarbons, 18, 31  
   acetylenes, 31  
   aromatic, 211, 213  
   hydroaromatic, 218  
   identification, 344  
   nitration, 213  
   olefins, 31

Hydrocarbons,  
 oxidation, 213  
 preparation, 211  
 properties, 213  
 reactions, 213  
 sources, 211  
 sulfonation, 213  
 unsaturated, 31  
 Hydrocarbons, saturated, 25  
 preparation, 27  
 properties, 27  
 Hydrocinnamic acid, 272  
 Hydrocyanic acid, 160, 228  
 Hydrogen cyanide, 160  
 Hydroquinone, 265  
 Hydroxy acids, 126  
 preparation, 126  
 properties, 127  
 Hydroxyazobenzene, *p*-, 246  
 Hydroxydimethylaniline, 284  
 Hydroxyquinoline, 308  
 Hypnone, 262  
 Hypoxanthine, 156

## I

Identification of compounds, 344  
 Indanthrene blue *R*, 324  
 Indican, 176, 309  
 Indigo, 309, 324  
 Indigo carmine, 312  
 Indole, 309  
 Indophenol blue, 322  
 Indoxyl, 309, 311  
 Indoxyl sulfuric acid, 309  
 Indoxylic acid, 311  
 Inner anhydrides, 125  
 Inner salts, 146  
 Inositol, 220  
 Insulin, 362  
 Intermediates, dyes, 226  
 Inulin, 181  
 Invertase, 358  
 Iodal, 82  
 Iodine number, 108  
 Iodochlorobenzene, *p*-, 228  
 Iodoform, 47  
 Iodol, 306  
 Iodotoluene, *p*-, 228

Isoamyl acetate, 102  
 Isoamyl alcohol, 63  
 Isoamyl isovalerate, 102  
 Isoamyl nitrite, 100  
 Isobutane, 24  
 Isocyanic acid, 164  
 Isocyanides, identification, 350  
 Isoelectric point, 144  
 Isoeugenol, 283  
 Isomerism, 21  
 anti-type, 261  
 cis-type, 95  
 optical, 128  
 stereo, 128  
 syn-type, 261  
 trans-type, 95  
 Isopentane, 24  
 Isophthalic acid, 273  
 Isoprene, 38, 332  
 Isopropyl alcohol, 63  
 Isoquinoline, 308  
 Isosuccinic acid, 94  
 Isovaleric acid, 91

## K

Karolith, 154  
 Kekulé, portrait, 204  
 Ketenes, 84  
 Ketones, 73  
 aromatic, 262  
 identification, 346  
 mixed, 75  
 nomenclature, 74  
 preparation, 75  
 simple, 75  
 Ketonic hydrolysis, 137  
 Knoop's  $\beta$ -oxidation theory, 189  
 Kolbe-Schmitt, reaction, 287

## L

Lacquers, 182  
 Lactase, 358  
 Lactic acid, 127, 128, 188  
 Lactones, 125  
 Lactose, 180  
 Lake, 316  
 Lanolin, 109, 111  
 Lead acetate, basic, 98

Lead tetraethyl, 199  
 Le Bel, 128  
 Lecithin, 110  
 Leucine, 147  
 Levulose, 177  
 Lewisite, 198  
 Lignoceric acid, 111  
 Limonene, 329  
 Linoleic acid, 92  
 Lipase, 358  
 Lipoids, 110  
 Luminal, 121  
 Lysine, 148

## M

Magnesium citrate, 133  
 Magnesium ethyl iodide, 199  
 Malachite green, 325  
 Maleic acid, 94, 130  
 Maleic anhydride, 94, 115  
 Malic acid, 126, 131  
 Malonamide, 122  
 Malonic acid, 93  
 Malonic ester, 103  
     uses, 103  
 Maltase, 358  
 Maltose, 180  
 Manna, 67  
 Mannans, 184  
 Mannitol, 67  
 Mannose, 178  
 Marsh gas, 18  
 Medicated alcohol, 62  
 Melanins, 356  
 Meldola's blue, 322  
 Mellitic acid, 275  
 Melting points, 382  
 Menthane, 330  
 Menthol, 330  
 Menthone, 330  
 Mercaptans, 194, 195  
     preparation, 195  
 Mercaptides, 195  
 Mercaptol, 196  
 Mercerized cotton, 181  
 Mercuric fulminate, 164  
 Mercuric salicylate, 342  
 Mercurochrome-220, 342

Mercury compounds, 338  
 Mesitylene, 216  
 Metaldehyde, 81  
 Metanilic acid, 281  
 Metaproteins, 151  
 Methane, 18  
     occurrence, 18  
     preparation, 18  
     properties, 19  
 Methanol, 58  
     chart, facing p. 58  
     preparation, 58  
     properties, 59  
     uses, 59  
 Methyl alcohol, 58  
 Methylaniline, 239  
 Methyl anthranilate, 290  
 Methylbenzene, 214  
 Methyl chloride, 44  
 Methyl cyanide, 161  
 Methyl glucoside, 176  
 Methylene blue, 323  
 Methylene iodide, 45  
 Methyl isocyanide, 162  
 Methyl isonitrile, 162  
 Methyl orange, 324  
 Methylphenylamine, 234  
 Methyl phenyl ether, 243, 251, 257  
 Methyl salicylate, 288  
 Metol, 284  
 Michler's ketone, 264  
 Millon's reaction, 153  
 Molisch, reaction, 153, 305  
 Monosaccharides, 167  
 Mordant, 316  
 Morphine, 337  
 Mucic acid, 305  
 Mucilages, 184  
 Muscarine, 110  
 Mustard gas, 196, 228  
 Myricyl alcohol, 63, 109  
 Myricyl palmitate, 103  
 Myronic acid, 176

## N

Naphthalene, 294  
 Naphthalene substituents, table, 300  
 Naphthalene sulfonic acid, 296, 297

Naphthalic acid, 298  
 Naphthionic acid, 299  
 Naphthoic acids, 298  
 Naphthol yellow S, 318  
 Naphthols, 297  
 Naphthoquinones, 299  
 Naphtholsulfonic acids, 299  
 Naphthylamine,  $\beta$ -, 298  
 Naphthylamine,  $\alpha$ -, 298  
 Naphthyl benzoate, 298  
 Naphthyl methyl ethers, 297  
 Naphthyl salicylate, 298  
 Narcotine, 337  
 Neosalvarsan, 341  
 Nerolin, 297  
 Nicotine, 336  
 Nitration, 213  
 Nitrile, 161  
 Nitroanilines, 278  
 Nitrobenzene, 231, 232  
 Nitrobenzoic acids, 270, 288  
 Nitrocellulose, 181  
 Nitro compounds, 164, 230  
     identification, 350  
     preparation, 231  
     properties, 232  
     reduction products, 232  
 Nitroethane, 44  
 Nitroglycerine, 101  
 Nitrolime, 161  
 Nitronaphthalenes, 297  
 Nitrophthalic acid, 295  
 Nitrophenols, 251, 279  
 Nitrosobenzene, 232  
 Nitroso compounds, 141  
 Nitrosodimethylamine, 165, 236  
 Nitrosodimethylaniline, 236, 239  
 Nitrosomethylaniline, 236  
 Nitroso- $\beta$ -Naphthol, 298  
 Nitrotoluenes, 231  
 Nobel, 66  
 Nomenclature, 363  
 Novocaine, 289  
 Nucleic acid, 155  
 Nuclein, 155  
 Nucleoproteins, 150, 155  
 Nucleoside, 155  
 Nujol, 29

## O

Octyl acetate, 102  
 Oil of anise, 286  
 Oil of bitter almonds, 260  
 Oil of caraway, 331  
 Oil of cinnamon, 262  
 Oil of cloves, 283  
 Oil of garlic, 196  
 Oil of lemon, 329  
 Oil of lime, 329  
 Oil of mirbane, 232  
 Oil of peppermint, 330  
 Oil of sassafras, 283  
 Oil of thyme, 254  
 Oil of turpentine, 329  
 Oil of wintergreen, 288  
 Oils, 105  
     essential, 333  
     hydrogenation, 107  
     properties, 108  
     table, 106  
 Olefins, 31  
 Oleic acid, 91  
 Olein, 105  
 Oleomargarine, 107  
 Optical activity, 128  
 Organic compounds, 2  
     analysis, 9  
     nomenclature, 363  
     purification, 7  
 Organic type formulas, facing p. 16  
 Organo-metallic compounds, 199  
 Osazones, 170  
 Osones, 170  
 Oxalic acid, 92  
     preparation, 92  
 Oxalyl chloride, 117  
 Oxamide, 121  
 Oxidation, 213

## P

Palmitic acid, 91  
 Palmitin, 99, 105  
 Paraffins, 18  
 Paraffin series, table, 26  
 Paraform, 80  
 Paraformaldehyde, 80  
 Paralactic acid, 129

- Paraldehyde, 81  
Parathyroid hormone, 362  
Parchment paper, 181  
Paris green, 98  
Pasteur, portrait, 130  
Pectins, 184  
Pentanes, 24  
Pentosans, 167  
Pentoses, 167  
Pepsin, 188, 358  
Peptones, 151  
Perkin, portrait, 315  
    reaction, 271, 309  
Peroxidase, 358  
Petrolatum, 29  
Petroleum, 18, 27, 28  
    cracking, 29  
    distillation, 28  
    distillation chart, facing p. 29  
    occurrence, 27  
    products derived, 28  
Phenacetin, 285  
Phenanthrene, 301, 303  
Phenetidine, 285  
Phenetole, 257  
Phenol, 243, 250  
    properties, 250  
Phenols, identification, 346  
Phenolphthalein, 274  
Phenolsulfonephthalein, 275  
Phenolsulfonic acids, 251, 281  
Phenoltetrachlorophthalein, 275  
Phenylacetaldehyde, 261  
Phenylacetate, 251  
Phenylacetic acid, 272  
Phenylacetylene, 217  
Phenyl alanine, 147  
Phenylcarbylamine chloride, 228  
Phenyl cyanide, 230  
Phenylenediamine, 240  
Phenyl ether, 257  
Phenylethyl alcohol, 249  
Phenylglycine, 312  
Phenylglycine-*o*-carboxylic acid, 311  
Phenylhydrazine, 169, 245  
Phenylhydroxylamine, 232  
Phenyl salicylate, 288  
Phloridzin, 176  
Phloroglucinol, 256  
Phosgene, 117, 228  
Phosphoproteins, 150  
Phosphorus compounds, 197  
Phrenosin, 111  
Phthalic acids, 273  
Phthalic anhydride, 273, 311  
Phthalimide, 273, 290, 311  
Phthalamidic acid, 311  
Phthalyl chloride, 274  
Phytosterol, 111  
Picramic acid, 280  
Picric acid, 279, 319  
Pigments, 353  
    animal, 355  
    plant, 353  
Pilocarpine, 337  
Pinene, 329  
Pinene hydrochloride, 329  
Piperidine, 307  
Piperine, 336  
Pituitrin, 362  
Polarized light, 128  
Polymers, 37  
Polypeptide, 151  
Polysaccharides, 167  
Potassium acid tartrate, 133  
Potassium antimonyl tartrate, 133  
Procaine, 290  
Proflavine, 313  
Prolamines, 150  
Proline, 150, 305  
Propane, 22  
Propanone, 74  
Propenol, 67  
Propine, 38  
Propionaldehyde, 74  
Propionic acid, 91  
Propylene, 35  
Protamines, 149  
Proteins, 151, 190  
    composition, 151  
    constitution, 151  
    identification, 351  
    reactions, 152  
Proteoses, 151  
Prussic acid, 160  
Ptyalin, 358

Purines, 156  
identification, 351

Putrefaction, 7

Putrescine, 142

Pyramidon, 306

Pyrazole, 306

Pyrazoline, 306

Pyrazolone, 306

Pyrene, 47

Pyridine, 307

Pyrimidine, 156

Pyrocatechol, 254

Pyrogallol, 255

Pyroligneous acid, 58, 90

Pyromucic acid, 305

Pyroxylin, 182

Pyrrole, 305

Pyrrolidine, 305

Pyruvic acid, 188

Pyruvic aldehyde, 187

## Q

Quaternary bases, 141

Quercetin, 355

Quinhydrone, 267

Quinine, 336

Quinol, 255

Quinoline, 307

Quinoline yellow, 322

Quinolmic acid, 308

Quinones, 264, 265

identification, 349

## R

Racemic acid, 132

Radicals, 363

Raffinose, 180

Rayon, 181

Red oil, 92

Reference Books, 384

Reimer-Tiemann, reaction, 286, 309

Remsen, portrait, 292

Rennin, 358

Resorcin, 254

Resorcin green, 318

Resorcinol, 254

Rhodamine B, 321

Rhodinal, 284

Ribose, 167

Rochelle salt, 133

Rosin, 329

Ruberythric acid, 177

Rules, substitution in the benzene ring, 215

## S

Sabatier and Senderens, reaction, 220

Saccharic acid, 174

Saccharin, 291

Safranine, 323

Safrole, 283

Salicin, 176

Salicyl alcohol, 285

Salicylaldehyde, 286

Salicylic acid, 287

Saligenin, 285

Salol, 288

Salts, 96

preparation, 97

properties, 97

Salvarsan, 338

Sandmeyer, reaction, 243

Saponification, 100, 102

Saponification number, 108

Sarcocollac acid, 129

Saturated hydrocarbon, 18, 25

nomenclature, 25

properties, 27

Schiff test, 82

Schweitzer's reagent, 181

Secretin, 362

Seidlitz powders, 133

Seliwanoff test, 178

Serine, 152

Silicon tetraethyl, 199

Silk, artificial, 181

Silver fulminate, 164

Skatole, 312

Skraup's reaction, 308

Smokeless powder, 184

Soaps, 98

Sodium benzenesulfonate, 229, 250

Sodium benzoate, 269

Sodium acetyl salicylate, 288

Sodium cinnamate, 272

Sodium citrate, 134



Sodium ethylate, 57  
 Sodium ethyl mercaptide, 194  
 Sodium formate, 98  
 Sodium palmitate, 99  
 Sodium phenolate, 229, 250  
 Sodium salicylate, 288  
 Sodium stearate, 99  
 Solubilities, 351  
 Sources of organic compounds, 5  
 Spermaceti, 109  
 Sphingomyelin, 111  
 Sphingosine, 111  
 Stains, 326  
 Starch, 180  
 Steapsin, 358  
 Stearic acid, 91  
 Stearin, 105  
 Stereoisomerism, 128  
 Stillbene, 217  
 Strychnine, 336  
 Styrene, 217  
 Substitution, 13, 20  
     rules, 215  
 Succinamide, 122  
 Succinic acid, 93, 95  
 Succinic anhydride, 94, 115  
 Succinimide, 122  
 Sucrase, 358  
 Sucrol, 285  
 Sucrose, 178  
 Sugar, 178  
 Sugar of lead, 98  
 Sulfanilic acid, 238, 280  
 Sulfarsenol, 341  
 Sulfides, 195  
     preparation, 195  
 Sulfoacetic acid, 197  
 Sulfobenzoic acid, 270, 290  
 Sulfonal, 196  
 Sulfonation, 213  
 Sulfonic acids, 228  
     identification, 347  
     preparations, 228  
     properties, 229  
 Sulfur black, 323  
 Sulfur compounds, 194  
     identification, 351  
 Sulfuric ether, 70

Sun yellow, 319  
 Sweet spirit of nitre, 100

## T

Tannic acids, 293  
 Tannins, 293  
 Tartar emetic, 133  
 Tartaric acid, 126, 131  
 Tartrazin, 319  
 Taurine, 197  
 Tautomerism, 135, 256  
 Terephthalic acid, 273  
 Terpenes, 328  
     identification, 351  
 Terpincol, 331  
 Tetrahydrobenzene, 218  
 Tetraiodophenolphthalein, 275  
 Tetralin, 299  
 Tetramethylammonium hydroxide,  
     141  
 Tetramethylmethane, 24  
 Tetraphenylethylene, 217  
 Tetryl, 231  
 Theine, 159  
 Theobromine, 159  
 Theophylline, 159  
 Thioacetic acid, 197  
 Thioacetone, 197  
 Thioacids, 195  
 Thioalcoholate, 194  
 Thiocarbamilide, 238  
 Thiophene, 306  
 Thiophenol, 229  
 Thiourea, 197  
 Thrombin, 358  
 Thymine, 156  
 Thymol, 254  
 Thyroxine, 361  
 Tin diethyl, 199  
 T. N. A., 231  
 T. N. T., 231  
 Tolane, 217  
 Toluene, 214  
 Toluenesulfonamide, 291  
 Toluenesulfonic acids, 228, 282, 291  
 Toluenesulfonyl chloride, 291  
 Toluic acids, 271  
 Toluidines, 239

Trans-form, 94  
 Tribromoaniline, 237  
 Tribromophenol, 250  
 Trichloroacetic acid, 123  
 Trichloromethyl chloro-formate, 228  
 Tricresol, 254  
 Triethanolamine, 141  
 Trimethylamine, 140  
 Trimethylarsine, 198  
 Trimethyl carbinol, 55  
 Trimethylphosphine, 198  
 Trinitrotoluene, 231  
 Trional, 196  
 Triphenylamine, 234  
 Triphenylguanidine, 238  
 Triphenylmethane, 217  
 Triphenylmethyl, 218  
 Triphenyl phosphate, 251  
 Trisaccharides, 167  
 Trithioacetaldehyde, 197  
 Tryparsamide, 342  
 Trypsin, 150, 188, 358  
 Cryptophan, 148, 312  
 Tyrosine, 148

## U

Uracil, 156  
 Urea, 119, 158  
     determination, 120  
     preparation, 119  
     properties, 120  
 Urease, 358  
 Urethane, 121  
 Uric acid, synthesis, 157  
 Urotropine, 80

## V

Valence, electronic conception, 11, 14  
 Valine, 147  
 Vanillin, 286  
 Van Slyke, 146  
 van't Hoff, 128  
 Verdigris, 98  
 Vinylacetylene, 40  
 Vinegar, 90  
 Viscose, 182  
 Vitamins, 359

## W

Waxes, 109  
 Williamson, synthesis, 69  
 Wohler, 1, 119  
 Wood alcohol, 58  
 Wurtz, synthesis, 21, 43

## X

Xanthic acid, 197  
 Xanthine, 157  
 Xanthoproteic, reaction, 153  
 Xanthophyll, 354  
 Xylenes, 216  
 Xylidine, 239  
 Xylose, 167  
 Xylol bromide, 228

## Y

Yara-yara, 297

## Z

Zinc ethyl, 199  
 Zinc methyl iodide, 199  
 Zymase, 358











